THE PHOTOLYSIS, RADIOLYSIS, AND MASS SPECTROMETRY
OF 1,1,2,2-TETRAFLUOROCYCLOBUTANE

By

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PREFACE

The decomposition dynamics of cyclobutane and substi-
tuted cyclobutanes have been investigated by numerous workers
under conditions of direct photolysis,[1,2] mercury sensitized
photolysis,[3,4] thermolysis,[5-7] radiolysis,[8-11] and electron
bombardment in the mass spectrometer.[12] A point of special
interest is the considerable ring strain in these compounds,
causing a propensity to undergo ring opening and fragmen-
tation into two ethylenic products. Even though the radiolysis
of both cyclobutane and perfluorocyclobutane has been studied,
no partially fluorinated cyclobutane has been investigated.
In fact, even the mass spectral cracking patterns of partially
fluorinated cyclobutanes have not been reported. However,
a study of the decomposition of such a compound would be very
interesting since it is expected to "bridge" the behavior of
cyclobutane and perfluorocyclobutane. Hence, we undertook
the study of the decomposition of 1,1,2,2-tetrafluorocyclo-
butane.

This work describes a study of the gas-phase gamma-
radiolysis of 1,1,2,2-tetrafluorocyclobutane (Chapter IV).
To help understand the energetics and mechanisms involved in
the radiolysis of this compound three additional investiga-
tions were carried out. They are:

(1) An electron impact investigation of 1,1,2,2-tetrafluorocyclobutane,* described in Chapter I.

(2) Ion-molecule reactions in 1,1,2,2-tetrafluorocyclobutane, described in Chapter II.

(3) Mercury $6(^3P_1)$ sensitized decomposition of 1,1,2,2-tetrafluorocyclobutane, described in Chapter III.

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THE PHOTOLYSIS, RADIOLYSIS, AND MASS SPECTROMETRY
OF 1,1,2,2-TETRAFLUOROCYCLOBUTANE

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Major Department: Chemistry

The fragmentation of 1,1,2,2-tetrafluorocyclobutane
under electron bombardment was investigated using a Bendix
Time-of-Flight mass spectrometer. Using the Fox Retarding
Potential Difference technique, measurements were made of
the appearance potentials of major ionic fragments including
$C_2H_2F_2^+$ (12.15 V), $C_2F_4^+$ (12.60 V), $C_2H_4^+$ (13.15 V), and $C_3H_4F^+$
(12.85 V). From these results it is found that ΔH_f^O for the
$C_3H_4F^+$ ion is $\leq$ +207 kcal/mole and ΔH_f^O for the parent $c\text{-}C_4H_4F_4$
is $\leq$ -202 kcal/mole. The symmetrical rupture of the molecule
into $C_2H_2F_2^+$ plus $C_2H_2F_2$ is a sequential process with the sum
of the energy of breaking two nonequivalent C-C bonds equal
to 126 kcal/mole, while the nonsymmetrical rupture into $C_2H_4^+$
and C_2F_4 is concerted, and the energy of breaking each of
the two equivalent C-C bonds between CF_2 and CH_2 groups is
61 kcal/mole.

To obtain kinetic data on the ion-molecule reactions in 1,1,2,2-tetrafluorocyclobutane, measurements of the variation of the ion intensities with the changes in delay time were carried out using a Bendix Time-of-Flight mass spectrometer. The parent ion $C_4H_4F_4^+$ had very low abundance and was found to be nearly non-reactive. However, ion-molecule reactions were observed for the olefinic ions $C_2H_2F_2^+$ and $C_2H_4^+$. It was found that $C_2H_2F_2^+$ becomes the most abundant ion in this system when the pressure is increased. Using the ICDR technique, it was established that reaction of $C_2H_2F_2^+$ with parent $c-C_4H_4F_4$ produces the species $C_6H_6F_6^+$ and $C_5H_6F_4^+$.

The Hg6($^3P_1$) photosensitized decomposition of 1,1,2,2-tetrafluorocyclobutane ($c-C_4H_4F_4$) was carried out by irradiating a mixture (50 or 150 Torr) of $c-C_4H_4F_4$ and mercury vapor with 253.7 nm radiation from a low pressure mercury lamp. The photolysis of a mixture of hydrogen and a small amount of $c-C_4H_4F_4$ was also investigated to establish the reactions of hydrogen atoms with $c-C_4H_4F_4$. Using the Chemical method of Cvetanovic, the quenching cross section of $c-C_4H_4F_4$ was determined to be 0.3 $\overset{o}{A}^2$ relative to that of N_2O.

Major products in the photolysis of the pure system include HF, two isomers of $C_6H_4F_6$, a C_8 compound, and $C_8H_6F_8$; the yields of these species and six others, formed in moderate quantities, were followed as a function of irradiation time.

It is suggested that the rupture of the C-H bond is the major primary process in the chemical quenching of Hg6($^3P_1$)

by 1,1,2,2-tetrafluorocyclobutane. A reaction scheme involving $C_4H_3F_4 \cdot$ and $H \cdot$ (formed in the primary quenching process), is proposed to explain the formation of the observed products.

The gamma-radiolysis of gaseous 1,1,2,2-tetrafluorocyclobutane was studied at 50 Torr pressure and 24^OC, both pure and with added oxygen. The major products were HF, H_2, 1,1-$C_2H_2F_2$, C_2F_4, C_2H_2, and $C_4H_3F_3$; C_2H_4 was seen only in the presence of oxygen. The addition of approximately 4% oxygen dramatically increased the G values of two olefins, 1,1-$C_2H_2F_2$ (from 0.046 to 0.47) and C_2H_4 (from ~0 to 0.125), decreased the yield of H_2, C_2F_4 and C_2H_2. Under the same conditions most heavier products were either eliminated or considerably reduced. The yield of $C_4H_3F_3$, however, was not changed substantially. Addition of both C_2H_4 and I_2 as scavengers decreased the yield of HF by 25%. The observations are interpreted in terms of reactions of both ions (especially $C_2H_2F_2^+$ and F^-) and neutral species.

CHAPTER I

AN ELECTRON IMPACT INVESTIGATION OF
1,1,2,2-TETRAFLUOROCYCLOBUTANE

Introduction

Information on the mass spectral cracking pattern of
a compound is very helpful to an understanding of its
radiolytic behavior, since slow electrons are responsible
for the decomposition in both the cases. Additionally, bond
energy data are very useful in interpreting the decomposition
dynamics of any compound. One reliable and accurate method
for obtaining bond energy information is the measurement of
appearance potentials of fragment ions of a compound in a
suitably equipped mass spectrometer using Retarding Potential
Difference (R.P.D.) techniques. The first goal of the present
investigation was to obtain the mass spectral cracking pattern
and bond dissociation energies in 1,1,2,2-tetrafluorocyclo-
butane (subsequently referred to as $c\text{-}C_4H_4F_4$)

$$
\begin{array}{ccc}
 & F & F \\
 & | & | \\
F- & C- & C-F \\
 & | & | \\
H- & C- & C-H \\
 & | & | \\
 & H & H
\end{array}
$$

since these data were not available.

Secondly, it has been proposed that the $c\text{-}C_4H_4F_4$ ion

1

constitutes the transition complex in ion-molecule reactions of $C_2H_2F_2^+$ with $C_2H_2F_2$, $C_2F_4^+$ with C_2H_4, and $C_2H_4^+$ with C_2F_4.[13,14] It was postulated that the complex is very short-lived and during its existance maintains its cyclic structure. Accordingly, a study of the fragmentation of this compound under electron impact is an obvious experiment to shed light on whether the predictions of the model are right and assumptions plausible.

In the present work, the appearance potentials of $C_2F_4^+$, $C_2H_4^+$, $C_2H_2F_2^+$, and $C_3H_4F^+$ from c-$C_4H_4F_4$ were measured. From these data we can calculate some of the bond dissociation energies in this compound and estimate some others. The experiments were done on a Time-of-Flight mass spectrometer using standard R.P.D. techniques.[15,16]

Experimental

The mass spectral cracking pattern of c-$C_4H_4F_4$ was obtained on the Bendix Time-of-Flight mass spectrometer at 70 eV. The R.P.D. experiments were also done on the Bendix, as described by Melton and Hamill[16] with some minor changes. Potentials on the five grid electron gun were as follows: No. 1 grid (electron control grid, nearest to the filament), -6 V with a +12 V pulse of 3 μsec duration repeated at a frequency of 10 kHz; No. 2 grid, +0.01 V; No. 3 grid (Fox retarding potential difference grid), -1.000 V with an intermittent ΔV of -0.200 V; No. 4 grid, +0.01 V; and No. 5 grid was grounded to the ion source structure (and therefore

to the frame of the instrument). Potentials on grids 1-4 are referenced to the electron filament, and hence their absolute value relative to ground varies along with the filament. The choice of -1.000 V for the Fox grid and -0.200 as ΔV was made after preliminary optimization experiments to obtain the best compromise of ion current I and its variation ΔI in response to ΔV applied to the R.P.D. grid. The purpose of the R.P.D. procedure is to measure an amount of ion current ΔI attributable to electrons in a narrow voltage range ΔV taken as a "slice" out of the much broader thermal electron energy distribution from the filament.

The ion focus pulse was triggered 0.7 μsec after the control grid pulse; we found this measure essential to obtaining reliable results. (It is possible to use the "time-lag-focusing" control for this purpose, on Bendix instruments so equipped.) The potential on the electron collecting trap was reduced to +8 V to minimize extraneous additional ionization of the experimental compound in the target region. Several minor modifications to the control electronics of the Bendix were made as recommended by Melton and Hamill.[16]

The ion current signal from the electrometer circuit in the "scanner" unit was fed to a potentiometric chart recorder through a potential divider. The compound under study was contained in a 5 ℓ. vessel and was leaked into the ionization chamber through a gold leak. The pressures in the ionization chamber could be changed by changing the pressure in the 5 ℓ. vessel. The usual operating pressure

in the ionization chamber was $6-8 \times 10^{-6}$ Torr. The normal trap current was 6 μA and the change in trap current was less than 5%. (The trap current was not regulated.)

The electron beam accelerating potential, which was applied to the filament, was generated by standard circuitry in the Bendix and monitored on the 40-V scale of a Digitec Model Z-204-B digital volt meter (resolution 0.005 V, accuracy 0.01 V). However, due to contact potentials, surface charges, etc., it can not be assumed that the effective accelerating potential of the electron gun is identical with that measured externally. Accordingly, an R.P.D. curve was measured for Ar^+ ion from argon gas and the apparent appearance potential of Ar^+ (corresponding to the first break) was determined from a graph made against the experimental voltage scale. The difference between the measured value and the accepted litera-ture value gave the necessary correction for the displacement of the voltage scale. Using the scale calibrated as described, cross checks were done by measuring the appearance potentials of $C_2F_4^+$ (from C_2F_4) and N_2^+ (from N_2). Our measured values agreed with the literature to within 0.1 V, indicating that our voltage scale is linear at least within the approximately 6-V range tested. In later experiments $C_2F_4^+$ and N_2^+ were used as secondary calibration standards.

We could reproduce exactly the shapes of ionization effi-ciency curves for CH_4^+ from CH_4 and $C_2H_6^+$, $C_2H_4^+$, and $C_2H_5^+$ from C_2H_6, which were reported by Melton and Hamill;[16] all re-ported "break points" agreed within a 0.1-V range. (The

CH_4^+ curve is shown in Figure 1.) Although we always had a moderate air background, N_2^+ (28) does not interfere with $C_2H_4^+$ (28) as the appearance potential of N_2^+ is 15.6 V and N_2^+ has zero intensity below about 15.1 V (well above the region of interest for $C_2H_4^+$). In the spectrum of c-$C_4H_4F_4$, the appearance potential of CH_2^+ could not be carried out because of the interference by the CH_2^+ in the background and that of CF_2^+ and $C_3H_3F_2^+$ could not be done because of very low intensities.

The 1,1,2,2-tetrafluorocyclobutane was obtained from Columbia Organic Chemicals Co. It was dried and deaerated on a vacuum line through several freeze-pump-thaw cycles at liquid nitrogen and Dry Ice temperatures, and vacuum distilled into a glass bulb for transfer to the mass spectrometer.

Results and Calculations

The Retarding Potential Difference curves which we obtained for $C_3H_4F^+$, $C_2H_2F_2^+$, $C_2F_4^+$, and $C_2H_4^+$ from c-$C_4H_4F_4$ are shown in Figures (1) and (2) along with N_2^+ as a standard and CH_4^+ for comparison with the work of Hamill and Melton.[16] The mass spectral fragmentation pattern which we obtained for c-$C_4H_4F_4$ is shown in Table I. In Table II we present the appearance potential values which were found for the several major product ions from c-$C_4H_4F_4$, along with values for certain other pertinent species from the literature.

From the appearance potential values given in Table II, along with the standard enthalpy of formation for several species from the literature[17-19] (given in Table III), it is
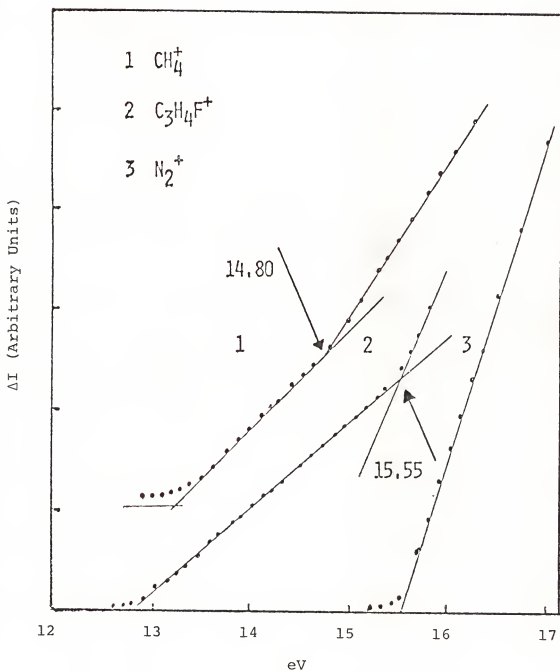
Figure 1. R.P.D. curves for CH_4^+ from CH_4, N_2^+ from N_2, and $C_3H_4F^+$ from $c-C_4H_4F_4$, measured on a Bendix T.O.F. mass spectrometer.
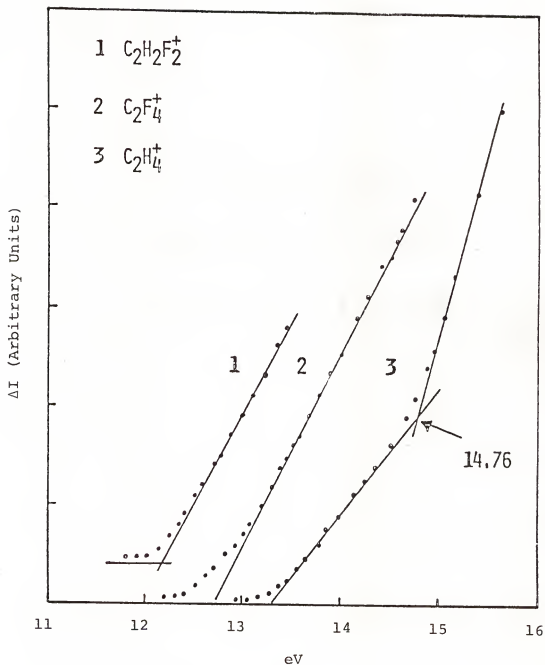
Figure 2. R.P.D. curves for $C_2H_2F_2^+$, $C_2F_4^+$, and $C_2H_4^+$ from $c\text{-}C_4H_4F_4$, measured on a Bendix T.O.F. mass spectrometer.

TABLE I

Mass Spectral Cracking Pattern of
c-$C_4H_4F_4$ at 70 V.

Mass	Intensity	Assignment	Mass	Intensity	Assignment
14	18	CH_2	57	7	C_3H_2F
16	7	CH_4	59	16	C_3H_4F
26	9	C_2H_2	64	100	$C_2H_2F_2$
27	11	C_2H_3	69	5	CF_3 or C_4H_2F
28	23	C_2H_4	75	4	C_3HF_2
31	13	CF	77	9	$C_3H_3F_2$
32	37	CHF	89	16	$C_4H_3F_2$
39	9	C_3H_3	100	23	C_2F_4
40	30	C_3H_4	109	9	$C_4H_4F_3$
44	12	C_2HF	113	3	C_3HF_4
45	18	C_2H_2F	127	2	$C_4H_3F_4$
50	6	CF_2	128	3	$C_4H_4F_4$
51	16	CHF_2			

TABLE II

Appearance Potential Data

Ion	Reactant	Product	AP
$C_2F_4^+$	$c\text{-}C_4H_4F_4$	$C_2F_4^+ + C_2H_4$	12.60 V^a
$C_2H_4^+$	$c\text{-}C_4H_4F_4$	$C_2H_4^+ + C_2F_4$	13.15 V^a
$C_2H_2F_2^+$	$c\text{-}C_4H_4F_4$	$C_2H_2F_2^+ + C_2H_2F_2$	12.15 V^a
$C_3H_4F^+$	$c\text{-}C_4H_4F_4$	$C_3H_4F^+ + CF_3$	12.85 V^a
$C_2H_4^+$	C_2H_6	$C_2H_4^+ + H + H$	16.3 V^b
$C_2H_4^+$	C_2H_4		10.48 V^c
$C_2H_2F_2^+$	$H_3C\text{-}CF_3$	$C_2H_2F_2^+ + HF$	10.30 V^c

[a]This work

[b]Melton and Hamill, Reference I.(16)

[c]NSRDS complilation, Reference I.(18)

TABLE III

Thermochemical Data

Ion or Radical	$\Delta H^{o}_{f\ 298}$ in Kcal/mole	Reference
$C_2F_4^+$	78	18
C_2H_4	12.49	18
$C_2H_4^+$	253	18
C_2F_4	−155.5	18
$C_2H_2F_2^+$	159	18
$C_2H_2F_2$	−78.6	18
CF_3	−112.6	19

possible to calculate heats of formation of the ion $C_3H_4F^+$ and the neutral parent molecule $c-C_4H_4F_4$, as well as values for the energy of dissociation of C-C bonds in the C_4 ring. The heat of formation of the parent molecule can be formulated in three different ways. First, using our measurements of the appearance potential of $C_2F_4^+$ we obtain:

$$c-C_4H_4F_4 \longrightarrow C_2F_4^+ + C_2H_4 + e^- \qquad \text{I.(1a)}$$
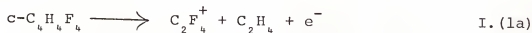
$$A(C_2F_4^+) \geq \Delta H_f^O (C_2F_4^+) + \Delta H_f^O (C_2H_4) - \Delta H_f^O (c-C_4H_4F_4) \qquad \text{I.(1b)}$$

Therefore

$$\Delta H_f^O (c-C_4H_4F_4) \geq \Delta H_f^O (C_2F_4^+) + \Delta H_f^O (C_2H_4) - A(C_2F_4^+) \qquad \text{I.(1c)}$$

$$\Delta H_f^O (c-C_4H_4F_4) \geq 78 \text{ kcal/mole} + 12.49 \text{ kcal/mole} - 12.60 \text{ eV} \qquad \text{I.(1d)}$$

$$\Delta H_f^O (c-C_4H_4F_4) \geq -200 \text{ kcal/mole} \qquad \text{I.(1e)}$$

Next, based on the appearance potential of $C_2H_4^+$ we can calculate:

$$c-C_4H_4F_4 \longrightarrow C_2H_4^+ + C_2F_4 + e^- \qquad \text{I.(2a)}$$
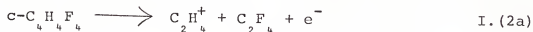
$$A(C_2H_4^+) \geq \Delta H_f^O (C_2H_4^+) + \Delta H_f^O (C_2F_4) - \Delta H_f^O (c-C_4H_4F_4) \qquad \text{I.(2b)}$$

Therefore

$$\Delta H_f^O (c-C_4H_4F_4) \geq \Delta H_f^O (C_2H_4^+) + \Delta H_f^O (C_2F_4) - A(C_2H_4^+) \qquad \text{I.(2c)}$$

$$\Delta H_f^O (c-C_4H_4F_4) \geq 253 \text{ kcal/mole} + (-155.5 \text{ kcal/mole} - 13.1 \text{ eV} \qquad \text{I.(2d)}$$

$$\Delta H_f^O (c-C_4H_4F_4) \geq -206 \text{ kcal/mole} \qquad \text{I.(2e)}$$

Finally, the measured appearance potential of $C_2H_2F_2^+$ gives

$$c\text{-}C_4H_4F_4 \longrightarrow C_2H_2F_2^+ + C_2H_2F_2 + e^- \qquad \text{I.(3a)}$$
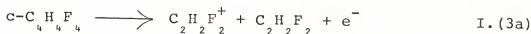
$$A(C_2H_2F_2^+) \geq \Delta H_f^O (C_2H_2F_2^+) + \Delta H_f^O (C_2H_2F_2) - \Delta H_f^O (c\text{-}C_4H_4F_4)$$
$$\text{I.(3b)}$$

Therefore

$$\Delta H_f^O (c\text{-}C_4H_4F_4) \geq \Delta H_f^O (C_2H_2F_2^+) + \Delta H_f^O (C_2H_2F_2) - A(C_2H_2F_2^+)$$
$$\text{I.(3c)}$$

$$\Delta H_f^O (c\text{-}C_4H_4F_4) \geq 159 \text{ kcal/mole} + (-79 \text{ kcal/mole}) -12.15 \text{ eV}$$
$$\text{I.(3d)}$$

$$\Delta H_f^O (c\text{-}C_4H_4F_4) \geq -200 \text{ kcal/mole} \qquad \text{I.(3e)}$$

Accordingly, the average value for $\Delta H_f^O (c\text{-}C_4H_4F_4)$ is $\geq$ -202 kcal/mole. The satisfactory agreement between the three calculations is gratifying because the calculations constitute a rather severe test of the consistency of the published thermochemical data as well as our appearance potential measurements.

Using our value of -202 kcal/mole for the heat of formation of $c\text{-}C_4H_4F_4$ and the appearance potential of $C_3H_4F^+$, we can calculate a value for the heat of formation of this ion as follows:

$$c\text{-}C_4H_4F_4 \longrightarrow C_3H_4F^+ + CF_3 \cdot + e^- \qquad \text{I.(4a)}$$
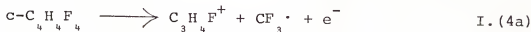
$$A(C_3H_4F^+) \geq \Delta H_f^O (C_3H_4F^+) + \Delta H_f^O (CF_3 \cdot) - \Delta H_f^O (c\text{-}C_4H_4F_4)$$
$$\text{I.(4b)}$$

Therefore

$$\Delta H_f^O \ (C_3H_4F^+) \ \leq \ A(C_3H_4F^+) \ - \ \Delta H_f^O \ (CF_3^{\cdot}) \ + \ \Delta H_f^O \ (c\text{-}C_4H_4F_4)$$

$$\text{I.(4c)}$$

$$\Delta H_f^O \ (C_3H_4F^+) \ \leq \ 12.85 \ eV - (-112.6 \ \text{kcal/mole}) + (-202 \ \text{kcal/mole})$$

$$\text{I.(4d)}$$

$$\Delta H_f^O \ (C_3H_4F^+) \ \leq \ +207 \ \text{kcal/mole} \qquad \text{I.(4e)}$$

In order to consider the energy of breaking C-C bonds in the c-$C_4H_4F_4$ ring, it is necessary to define our notation. First, we let $D_{(F/F)}, D_{(H/H)},$ and $D_{(H/F)}$ be the bond dissociation energy of the bonds shown below. (Note that $D_{A/B}$ represents a C-C dissociation energy of a bond where "A" and "B" are substituents on the carbon atoms.)
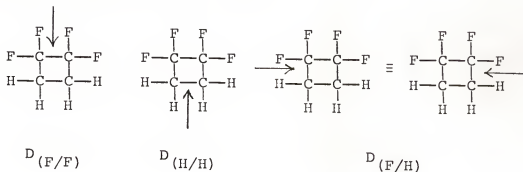
We also let $\Delta H_{(=H/H)}$ and $\Delta H_{(=H/F)}$ represent the energies for the _reverse_ of the following processes:

$$\text{I.(5)}$$

$$\text{I.(6)}$$
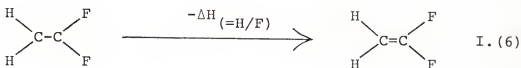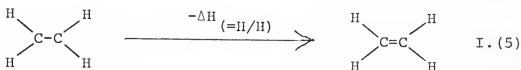
In order to determine the enthalpy change in these reactions,

useful energy cycles can be written as follows:

$$\text{H}_3\text{C}-\text{CH}_3 \xrightarrow{2D_{C-H}} \cdot\text{CH}_2-\text{CH}_2\cdot \ + \text{H} + \text{H} \qquad \text{I.(7)}$$

$$\Big\downarrow -\Delta H_{(=H/H)} \qquad \text{I.(8)}$$

$$\text{H}_2\text{C}=\text{CH}_2 \xrightarrow{I_{(C_2H_4^+/C_2H_4)}} \text{C}_2\text{H}_4^+ + \text{e}^- \qquad \text{I.(9)}$$

and

$$\text{CHF}_2-\text{CH}_2\text{F} \xrightarrow{D_{C-H} + D_{C-F} - D_{H-F}} \cdot\text{CHF}-\text{CHF}\cdot \ + \text{HF} \qquad \text{I.(10)}$$

$$\Big\downarrow -\Delta H_{(=F/H)} \qquad \text{I.(11)}$$
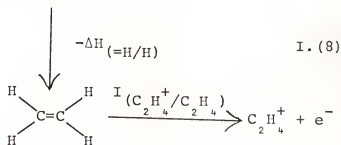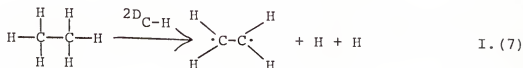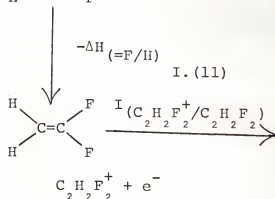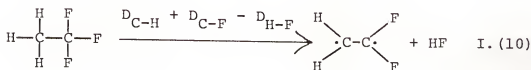
$$\text{CHF}=\text{CHF} \xrightarrow{I_{(C_2H_2F_2^+/C_2H_2F_2)}} \text{C}_2\text{H}_2\text{F}_2^+ + \text{e}^- \qquad \text{I.(12)}$$

where D_{C-H} is the C–H bond dissociation energy in C_2H_6, or $C_2H_3F_3$, D_{C-F} is the C–F bond dissociation in CH_3CF_3, and D_{H-F} is the H–F bond dissociation energy (equal to the bond energy in this case). We will use $I_{(C_2H_4^+/C_2H_4)}$ to indicate the ionization potential (or appearance potential) of $C_2H_4^+$ from

C_2H_4 and similarly for other daughter ion/parent molecule pairs which are mentioned subsequently.

Then we have

$$A(C_2H_4^+/C_2H_6) = 2D_{C-H} - \Delta H_{(=H/H)} + I(C_2H_4^+/C_4H_4) \quad \text{I.(13)}$$

$$A(C_2H_2F_2^+/C_2H_3F_3) = D_{C-H} + D_{C-F} - D_{H-F} - \Delta H_{(=F/H)} +$$

$$I(C_2H_2F_2^+/C_2H_2F_2) \quad \text{I.(14)}$$

Therefore, application of the energy cycle (I.(7)-I.(9)) to Reaction I.(5) gives

$$\Delta H_{(=H/H)} = 2D_{C-H} + I(C_2H_4^+/C_2H_4) - A(C_2H_4^+/C_2H_6) \quad \text{I.(15)}$$

$$\Delta H_{(=H/H)} = 2(4.16) + 10.48 - 16.3 = 2.5 \text{ eV} \quad \text{I.(16)}$$

A similar calculation for Reaction I.(6) using the energy cycle (I.(10)-I.(12)) gives:

$$\Delta H_{(=H/F)} = D_{C-H} + D_{C-F} - D_{H-F} + I(C_2H_2F_2^+/C_2H_2F_2)$$

$$-A(C_2H_2F_2^+/C_2H_3F_3) \quad \text{I.(17)}$$

$$= (4.16 + 4.6 - 5.82 + 10.12 - 11.2) = 1.86 \text{ eV} \quad \text{I.(18)}$$

It would be of interest to calculate the quantity $\Delta H_{(=F/F)}$ for formation of tetrafluoroethylene from the corresponding diradical, but the necessary data are not accessible - $C_2F_4^+$ has zero abundance from C_2F_6 and C_2F_5H.[20]

We next consider the energetics of the unsymmetrical splitting of c-$C_4H_4F_4$ into $C_2H_4^+$ and C_2F_4:

$$\text{c-}C_4H_4F_4 \longrightarrow C_2H_4^+ + C_2F_4 + e^- \quad \text{I.(19)}$$
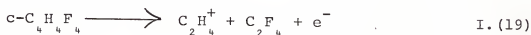
It is possible to make two reasonable, limiting assumptions about the energetics of this process (and the similar symmetrical split into $C_2H_2F_2^+$ and $C_2H_2F_2$): either the reorganization of the neutral fragment into a double-bonded species occurs before the split from the ion, or else it occurs afterwards. If the latter is the case, then the corresponding reorganization energy is not available to decrease the energy of formation of the observed ionic fragment:

$$A(C_2H_4^+/c\text{-}C_4H_4F_4) = 2D_{(F/H)} - \Delta H_{(=H/H)} + I(C_2H_4^+/C_2H_4)$$

$$\text{I.(20)}$$

This assumption leads to the following evaluation of $D_{(F/H)}$, the energy per bond to break the $CF_2 \ldots CH_2$ carbon-carbon bonds in the $c\text{-}C_4H_4F_4$ ring:

$$2D_{(F/H)} = \Delta H_{(=H/H)} - I(C_2H_4^+/C_2H_4) + A(C_2H_4^+/c\text{-}C_4H_4F_4)$$

$$\text{I.(21)}$$

$$2D_{(F/H)} = 2.5 \text{ eV} - 10.48 \text{ eV} + 13.25 \text{ eV} \qquad \text{I.(22)}$$

and

$$D_{(F/H)} = 2.64 \text{ eV} = 61 \text{ kcal/mole} \qquad \text{I.(23)}$$

The magnitude of the resulting bond dissociation energy appears reasonable; the significance of this result will be considered further in the Discussion section.

In the case of the symmetrical dissociation process, the alternative limiting assumption appears to give reasonable results:

$$c\text{-}C_4H_4F_4 \longrightarrow C_2H_2F_2^+ + C_2H_2F_2 \qquad \text{I.(24)}$$
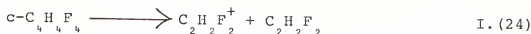
Assuming that all of the reorganization energy is available to drive the process, we obtain:

$$A(C_2H_2F_2^+/c\text{-}C_4H_4F_4) = D_{(F/F)} + D_{(H/H)} - 2\Delta H_{(=F/H)}$$
$$+ I(C_2H_2F_2^+/C_2H_2F_2) \qquad \text{I.(25)}$$

which rearranges to give

$$D_{(F/F)} + D_{(H/H)} = A(C_2H_2F_2^+/c\text{-}C_4H_4F_4) + 2\Delta H_{(=F/H)}$$
$$- I(C_2H_2F_2^+/C_2H_2F_2) \qquad \text{I.(26)}$$

$$D_{(F/F)} + D_{(H/H)} = 12.05\,\text{eV} + 2(1.86\,\text{eV}) - 10.30\,\text{eV} \qquad \text{I.(27)}$$

$$D_{(F/F)} + D_{(H/H)} = 5.47\,\text{eV} = 126\,\text{kcal/mole} \qquad \text{I.(28)}$$

Accordingly, the average of these two bond dissociation energies is the reasonable value of 63 kcal/mole. This result will also be considered in the Discussion.

In order to carry out a calculation for the third dissociation process, into $C_2F_4^+$ and C_2H_4, we would need the energy of a tetrafluoroethylene diradical rearranging to tetrafluoroethylene. As noted above, we were not able to calculate this quantity.

Discussion

The overall mass spectral fragmentation pattern of $c\text{-}C_4H_4F_4$ is consistent with what might be expected for a saturated, cyclic C_4 compound.[21] Most compounds of this type

give a small parent peak along with considerable fragmentation
into lower molecular weight ions. Furthermore, Jennings[13]
has postulated that the cyclic $C_4H_4F^+$ ion, formed as an
intermediate complex in several ion-molecule reactions, has
a very short lifetime. It appears reasonable to suggest that
the structure of the $c-C_4H_4F^+$ system reached upon electron
bombardment of the stable molecule is the same one formed in
the ion-molecule reactions, although there could be differences
in internal energies (especially vibrational energy). We note
that $c-C_4H_4F_4$ shows a small abundance of the parent ion,
$c-C_4H_4F_4^+$; this is consistent with the fact that Jennings
also saw a small amount of $c-C_4H_4F_4^+$ at high pressures (pre-
sumably, involving some collisional stabilization in the ion-
molecule experiments).

As can be seen from the cracking pattern of $c-C_4H_4F_4$,
there is no peak corresponding to $C_2H_3F^+$ or $C_2HF_3^+$. This fact
lends some credibility to the assumption made by Jennings
that the transition complex formed in the systems $[1,1-CF_2CH_2]^+$
on $1,1-C_2H_2F_2$, $C_2H_4^+$ on C_2F_4, and $C_2F_4^+$ on C_2H_4 maintains a
stable structure and does not scramble F and H atoms during
its brief existence. We note a number of species which must
involve some rearrangement, however, such as CHF^+. It is our
suggestion that most (and perhaps all) such rearrangement
occurs in connection with ring opening, which produces un-
saturated carbon centers.

We calculate the heat of formation of $c-C_4H_4F_3^+$ to be
about 190 kcal/mole by Franklin's group contribution method.[22]

This value, when combined with our value for ΔH_f^O of c-$C_4H_4F_4$, gives 14.4 V for the appearance potential of $C_4H_4F_3^+$ if we assume concurrent elimination of F^-, and a value of 18.0 V if we assume F atom elimination. We find an approximate appearance potential of c-$C_4H_4F_3^+$ of 13.5 ± 1 V. Although our data were not of high quality, due to the low abundance of the ion, its appearance potential is certainly not higher than 15.0 V. Accordingly, we conclude that c-$C_4H_4F_3^+$ is formed by F^- elimination.

The two modes of splitting the cyclobutane ring into an ethylenic ion and an ethylenic molecule (Reactions I.(19) and I.(24)) clearly must proceed by two different mechanisms. For the unsymmetrical break (Reaction I.(19)) we utilized in the calculation only the reorganization energy of $\cdot CH_2CH_2\cdot$ into C_2H_4, and obtained 61 kcal/mole each for breaking two $CF_2 \ldots CH_2\cdot$ bonds. If we had also utilized the reorganization energy of $\cdot CF_2CF_2\cdot$ into $CF_2{=}CF_2$ the resulting bond dissociation energies would increase by at least 15 to 20 kcal each, which would surely be too high for the badly strained c-$C_4H_4F_4$ molecule.

On the other hand, we utilized the reorganization energy for two $\cdot CF_2CH_2\cdot$ fragments into $CF_2{=}CH_2$, in order to interpret the data for the symmetric split. We obtained 126 kcal for $D_{(F/F)}$ plus $D_{(H/H)}$, or an average of 63 kcal/mole for dissociation of $CF_2 \ldots CF_2$ and $CH_2 \ldots CH_2$, which is of a reasonable magnitude. (If we apportion the two energies similar to the known dissociation energies of $CF_3 \ldots CF_3$ and $CH_3 \ldots CH_3$, the

resulting values are 57 kcal/mole and 69 kcal/mole respectively.) Use of only one reorganization energy term would give an impossibly low value of 46.5 kcal/mole for the average of $D_{(F/F)}$ and $D_{(H/H)}$. In fact, the postulate that anything much less than 100% of the two reorganization energy terms is available to drive Reaction I.(24) would lead to an unrealistically low result.

Our specific suggestion for the mechanistic difference in Reactions I.(19) and I.(24) (which forms the foundation of the different energetics) is that the former is a one-step dissociation giving $C_2H_4^+$ and an energy-rich $\cdot CH_2CF_2 \cdot$ species (which later forms $CF_2=CF_2$ without aiding in the progress of the original dissociation) while Reaction I.(24) is sequential, proceeding through an open-chain intermediate.

$$\text{I.(24a)}$$

$$\text{I.(24b)}$$
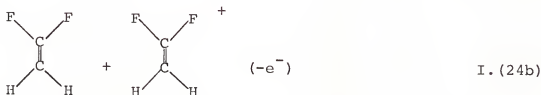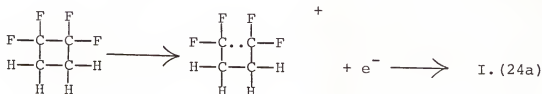
Consistent with the conclusions reached by Jennings et al., as well as our own observations, the open-chain species formed in Reaction I.(24a) would have to be short-lived (10^{-6} sec or less). Atom-migration in the open-chain intermediate could explain occurrence of several additional species in the

cracking pattern of c-$C_4H_4F_4$, in particular CF_3^+ and $C_3H_4F^+$. A similar ring-opening of $C_4H_4F_3^+$ followed by a split into 1-carbon and 3-carbon fragments would explain the occurrence of CFH^+ (37%) and $C_3H_3F_2^+$ (9%). Several other similar decomposition sequences can be suggested.

The more favorable reaction path and energetics leading to $C_2H_2F_2^+$ compared to $C_2H_4^+$ (and probably also $C_2F_4^+$) are very likely related to the relative abundances of 100%, 23%, and 23% for these three species. Although the intensity of $C_2H_2F_2^+$ should equal the sum of the intensities of $C_2F_4^+$ and $C_2H_4^+$ due to statistical considerations, it is in fact even higher by a factor of two.

Our appearance potential value (12.85 V) for the $C_3H_4F^+$ ion gives a value of 207 kcal/mole for ΔH_f^O of this species, which is closer to a previously reported experimental value of 210 kcal/mole than to a theoretically estimated value of 175 kcal/mole.[23] The calculated ΔH_f^O is apparently for a linear species; we suggest that the $C_3H_4F^+$ species formed in this work may have a cyclopropane structure. (Other C_3 species formed might also be cyclic.)

The utility of the electron impact method for determining thermodynamic quantities rests on the implicit assumption that the relevant but unmeasured corrections for excess energy in ionic and molecular fragments are small.[16-18,24] This situation is recognized by inequality signs in Equations I.(1)–I.(4). In several instances (see Equations I.(15), I.(17), I.(21), and I.(26)) two ionization or appearance potential

terms enter with opposite signs, so that partial cancellation of excess energy effects can be expected. (In these cases no inequality is indicated since its sign is not unambigous.) An assumption of little or no excess energy is supported by Stevenson's Law[25] in the case of $C_2F_4^+$ and $C_2H_4^+$, since the appearance potential of $C_2F_4^+$ is 0.55 V less than that of $C_2H_4^+$. This argument is not applicable in the case of $C_2H_2F_2^+$, but the good agreement of ΔH_f^O (c-$C_4H_4F_4$) from Equations I.(1), I.(2), and I.(3) suggests that any excess energy correction needed for $A(C_2H_2F_2^+)$ must be small in the latter case as well; our results suggest that ΔH_f^O (c-$C_4H_4F_4$) = -202 kcal/ mole with little or no correction required for excess energy.

Although the R.P.D. curves for $C_3H_4F^+$ and $C_2H_4^+$ both show well-defined breaks at higher energies (respectively 2.70 and 1.61 V above the appearance potentials) we have not attempted to interpret the electronic states or processes involved. However, Hamill and coworkers have had considerable success in understanding data of this type.[26]

CHAPTER II

ION-MOLECULE REACTIONS IN
1,1,2,2-TETRAFLUOROCYCLOBUTANE

Introduction

This work was undertaken to obtain supplementary
information on ionic reactions in the gamma-radiolysis of
gaseous 1,1,2,2-tetrafluorocyclobutane. Most of the
reactions leading to stable products in the radiolysis
of this compound appear to be radical reactions or molecular
elimination processes. These radicals may have ionic pre-
cursors, however, since one of the major primary events in
the gamma-radiolysis is the ionization of the compound.
Accordingly, examination of ion-molecule reaction pathways
in this system, using the technique of high pressure single
source mass spectrometry and ion cyclotron resonance mass
spectrometry, can shed light directly on the mechanism of
the radiolytic decomposition.

Experimental

In this investigation the following two kinds of ex-
periments were carried out using two different instruments:
(1) measurement of the variations of the ion intensities as
a function of delay time (i.e., delay between ion generation

and ion extraction for detection) using a Bendix Time-of-Flight mass spectrometer and (2) investigation of the reaction pathways using the ion cyclotron double resonance (ICDR) technique in a Varian "Synotron" ion cyclotron resonance instrument.

The Bendix Time-of-Flight mass spectrometer (model 14-107) was modified as described by Futrell et al.[27] The electron energy was 100 eV. Ion grid No. 1 was at +18 V and the repeller grid at +6 V with respect to ground. Distance from the repeller grid to exit orifice was 0.533 cm, and the drift distance from the electron beam position to the exit orifice was 0.267 cm. Under these conditions the field strength in the reaction chamber is 11.25 V/cm. A new circuit shown in Figure (3) was used to provide a positive pulse to ion grid No. 1. This circuit provided for the variation of the pulse height from 0 to +25 V and the width from 2 to 6 μsec while maintaining a very fast rise time (ca. 2 nsec) and very short delay (<1 nsec) relative to the ion focus pulse. In the experiments reported here the pulse height was at +23 V and the width was 4 μsec. All other ion source potentials were identical to those reported by Futrell.[27] Further details about setting up and adjusting the instrument were described by Heckel and Hanrahan;[28] similar procedures were employed in the present work. All ion intensity measurements taken under the pulsed conditions were corrected for diffusional discrimination using as a correction term the inverse square root of the ion mass $(1/\sqrt{m})$.[27,29] Mass
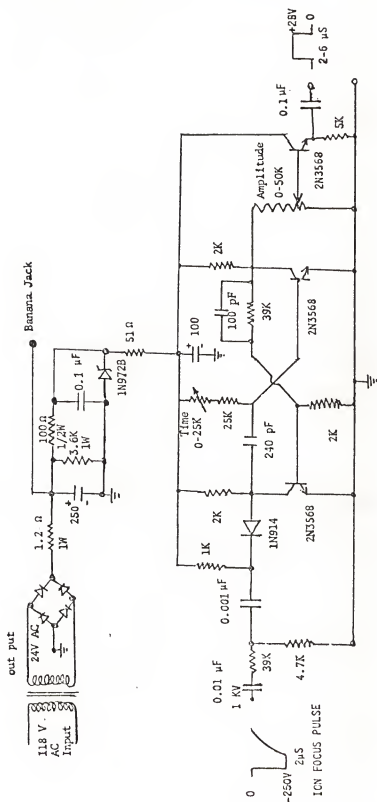
Figure 3. Circuit diagram of the pulse generator for ion grid Number 1.

spectrometric data acquisition and data reduction, including
the square root correction, were carried out using a General
Automation SPC-12 mini-computer as described in a previous
report.[30]

The ion source was operated at 50° C. The reactant
c-$C_4H_4F_4$ gas was leaked into the ion source through a gold
leak from a 5 ℓ. reservoir. Variation of the reservoir
pressure allowed adjustment of the pressure in the ion
source, which was monitored using an MKS Baratron capacitive
micromanometer (model 77) equipped with a 3 mm head. The
tetrafluorocyclobutane was obtained from Columbia Organic
Chemicals, Columbia, South Carolina, and was purified by
trap-to-trap distillation.

Ion cyclotron resonance experiments were carried out
on a Varian "Synotron" (model 5900) equipped with a flat cell.
In the ion cyclotron double resonance (ICDR) experiments the
second radio frequency field was applied to the source region.
The procedure described by Jennings[31] was followed to obtain
the double resonance signals.

Results

It is possible to obtain rate data in a suitably equipped
single-source mass spectrometer using a time delay mode, as
originally described by Tal'roze.[32] In this procedure ions
are generated by a brief electron pulse (ca. 1 μsec wide),
allowed to react with the substrate gas for an appropriate
time (typically 1 to 10 μsec), and then extracted for analysis

by a pulse delayed with respect to the electron pulse.[33]

The procedure in our instrument is substantially the same, except that a small portion of the reactant gas - product ion mixture from the source region continually effuses from the exit orifice, and these effusing ions are sampled by the ion focus pulse at a specified, variable delay time after the electron pulse.[29,34] In either event, the ions undergo a pseudo-first order reaction with the substrate gas. A plot of the log of the normalized, corrected ion intensity versus delay time gives a straight line with slope equal to the pseudo-first order rate constant; multiplying by the ambient gas number density (molecules/cc) gives the second order rate constant directly.

Figure (4) shows the variation of the normalized, square root corrected intensities of five ions, $C_2H_4^+$, $C_2H_2F_2^+$, CF^+, $C_2F_4^+$, and $C_4H_4F_3^+$, as a function of delay time at a pressure of 27 microns. (Smooth curves through the experimental data points in Figures (4), (5), and (6) are visual best fits.) Intensities of $C_2H_4^+$ and CF^+ decay to zero within 3 μsec and $C_2H_2F_2^+$ intensity grows to a near constant value at approximately 3 μsec. After 3 μsec $C_2F_4^+$ and $C_2H_2F_2^+$ ion intensities continue to grow, while the abundance of $C_2H_2F_2^+$ levels off and declines somewhat. A similar plot is obtained at a pressure of 53 microns as shown in Figure (5). Semilogarithmic plots of normalized, corrected intensities for loss of $C_2H_4^+$ and CF^+, and formations of $C_2H_2F_2^+$, $C_2F_4^+$, and $C_4H_4F_3^+$, measured at $50°$ C against delay time gave good straight lines; resulting rate
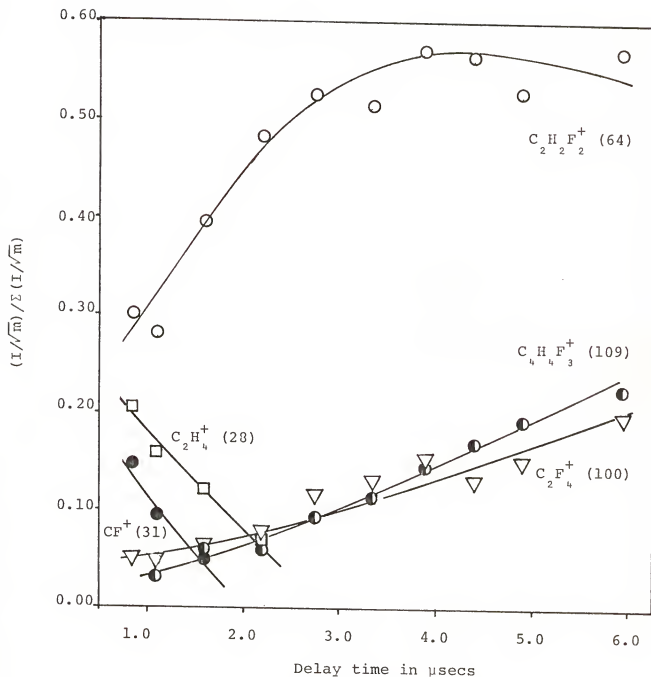
Figure 4.   Normalized ion intensities as a function of delay
time in the T.O.F. spectrum of 1,1,2,2-tetra-
fluorocyclobutane at 26.8 microns and 50° C.
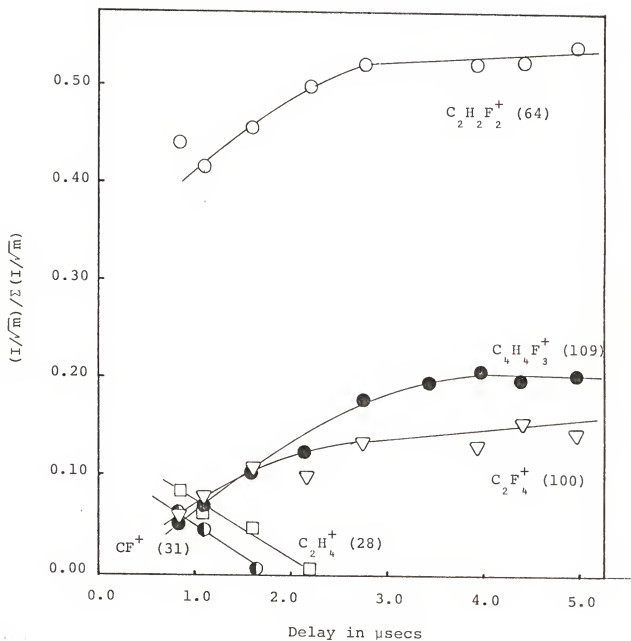
Figure 5.   Normalized ion intensities as a function of delay time in the T.O.F. spectrum of 1,1,2,2-tetrafluorocyclobutane at 53.0 microns and 50° C.

constants (based on a linear least squares fit of the data points) are given in Table 1V.

It is also possible to obtain ion-molecule reaction rate data in a single source instrument using the classical pressure variation method. This technique consists of measuring the ion intensities as a function of pressure in the presence of a known field strength, produced by the repeller grid. Although ion-molecule rate data were first taken using the pressure variation method, there are difficulties with interpreting the results of this procedure.[28,35] When continuous ionization is used, the essence of the problem is that the effective reaction time for light ions is shorter than for heavy ions, since the former are lost sooner in collisions with the wall. By operating our instrument at a fixed, intermediate value of the ion-extraction delay parameter, it is possible to mitigate this difficulty to some extent; most intermediate and heavy mass ions then have the same effective reaction time, while some but not all of the light ions are lost. By operating in this manner with a fixed delay of 1.6 μsec we were able to take pressure dependence data which gave a reasonable comparison to the time-delay data, without recourse to extensive diffusion calculations.[28] Results thus obtained are shown in Figure (6); the rate constants are shown in Table IV.

Several ionic species observed in the Bendix instrument had intensities too low for quantitative work. Many of these (CHF^+, $C_3H_3^+$, etc.) are fragment ions which apparently disappear

TABLE IV

Rate Constants for Ion-Molecule Reactions
in 1,1,2,2-Tetrafluorocyclobutane

Reaction	Pressure in Microns	Rate Constant in cc molecule^{-1} sec^{-1} x 10^{10}	Method[a]
Disappearance of $C_2H_4^+$	26.8	11.0	TD
	53.0	7.76	TD
		16.2	PD
Disappearance of CF^+	26.8	17.9	TD
	53.0	11.4	TD
		17.7	PD
Formation of $C_2H_2F_2^+$	26.8	4.3	TD
	53.0	0.89	TD
		1.74	PD
Formation of $C_2F_4^+$	26.8	5.1	TD
	53.0	2.9	TD
		3.4	PD
Formation of $C_4H_4F_3^+$	26.8	7.5	TD
	53.0	4.0	TD
		5.2	PD

[a]TD = Rate constants obtained from the time delay experiments.
 PD = Rate constants obtained from the pressure dependence
   experiments.
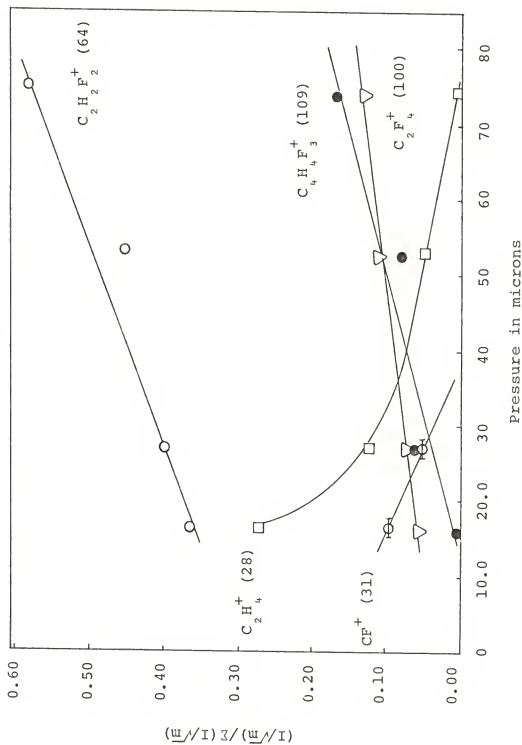
Figure 6. Normalized ion intensities as a function of pressure in the T.O.F. spectrum of 1,1,2,2-tetrafluorocyclobutane at 250° C.

by reaction with the substrate. Of more interest, however, are two ions with molecular weights greater than the parent molecule; the species appear at m/e 164 ($C_4H_2F_6^+$) and 192 ($C_6H_6F_6^+$). The former ion is formed with moderate intensity under conditions of very low repeller grid voltage; it is formed in an ion-molecule reaction in which an ion of m/e 64 ($C_2H_2F_2^+$) is consumed by reaction with the substrate. Although no further information on the ion of mass 192 was obtained using the Bendix instrument, its mode of formation was characterized by the ICDR technique described below.

In the original ion cyclotron method for the observation of ion-molecule reaction as developed by Baldeschweiler, an investigation of the variation of ion intensities as a function of pressure also allows calculation of rate constants.[36] Although we investigated the ICR spectrum of 1,1,2,2-tetrafluorocyclobutane over the entire pressure range available on the Varian instrument, no variation in ion intensities was observed. (The instrument operates well at pressures from 1×10^{-4} Torr to 1×10^{-6} Torr; although the region 1×10^{-7} Torr is accessible, the poor signal-to-noise ratio prevents quantitative measurements in this region.) Throughout the readily accessible pressure region, the spectrum observed on the ICR instrument resembles high-pressure or long delay-time spectra seen using the Bendix machine. Apparently due to the very long residence times in the ICR instrument (several milliseconds), the more reactive ions, such as ethylene in the present case, have already reacted.

A more recent technique using the ICR instrument is the double resonance method, in which kinetic energy of a chosen reactant ion is enhanced by irradiation with a second radio frequency field. The product ion intensity will increase provided the formation reaction of the product ion is endoergic. However, a decrease in the product ion intensity with an increase in the kinetic energy of the reactant ion indicates either an exoergic or thermoneutral reactions. Such a decrease in intensity is most commonly seen in exoergic reactions.

In the ICR instrument two ions heavier than the parent ion, one at m/e of 192 and the other at m/e of 142, were formed above 6×10^{-6} Torr. Although the ion with m/e of 192 ($C_6H_6F_6$) was seen in experiments carried out using the Bendix machine, the ion of m/e 142 ($C_5H_6F_4$) was not seen probably due to a very low formation rate constant. Using the ICDR technique, the reactant ion in the formation reactions of these two heavier ions was established to be $C_2H_2F_2^+$. The ICDR signal for the reactions leading to the formation of $C_6H_6F_6^+$ and $C_5H_6F_4^+$ at different power-levels of the second radio frequency field, applied to the source region, were of the shapes shown below (vertical axis, intensity; horizontal axis, double resonance frequency):

(For ion with m/e of 192)   (For ion of m/e of 142)

The power absorption by the product ions decreases when the
intensity of the second radio frequency field of frequency
corresponding to that of $C_2H_2F_2^+$ is increased, indicating
that both the reactions are exoergic.

Discussion

An examination of the low pressure mass spectrum of
c-$C_4H_4F_4$ (Table V) shows that the compound fragments ex-
tensively under electron impact. The six most intense ions
are all C_1 and C_2 fragments (abundancies from 33% down to
ca. 6%). The parent $C_4H_4F_4^+$ ion (not necessarily cyclic)
has an abundance of only 0.1%; the other C_4 species, $C_4H_4F_3^+$
and $C_4H_3F_2^+$, occur to the extent of 2.9 and 5.3%, respectively.
In all, five C_3 fragments are seen, but the abundance of the
most important is only 5.3%.

In previous researches by Jennings et al.[13,14] and
Anicich and Bowers[37] the ion $C_4H_4F_4^+$ was formed by the reaction
of an ethylenic ion ($C_2H_2F_2^+$, $C_2H_4^+$, or $C_2F_4^+$) on an ethylenic
target molecule ($C_2H_2F_2$, C_2F_4, or C_2H_4, respectively). It
was found that the intermediate complex ion $C_4H_4F_4^+$ is very
unstable (life time < 2 μsec) and decomposes unless col-
lisionally stabilized. The major products are an ethylenic
ion/ethylenic molecule pair:

$$C_4H_4F_4^+ \longrightarrow C_2H_2F_2^+ + C_2H_2F_2 \qquad \text{II.(1a)}$$

$$C_4H_4F_4^+ \longrightarrow C_2H_4^+ + C_2F_4 \qquad \text{II.(1b)}$$

$$C_4H_4F_4^+ \longrightarrow C_2F_4^+ + C_2H_4^+ \qquad \text{II.(1c)}$$

TABLE V
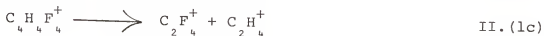
Mass Spectral Fragmentation Patterns of 1,1,2,2-Tetrafluorocyclobutane Under Analytical and Ion-Molecule Reaction Conditions

m/e	Assignment	Low Pressure Spectrum[b]	Intensity[a]				ICR Spectrum at 6.5 x 10^{-5} Torr[d]
			High Pressure Spectrum[c]				
			27 Microns		53 Microns		
			Short Time	Long Time	Short Time	Long Time	
12	CH_2	5.8					
27	C_2H_3	4.1	7.0		5.1		
28	C_2H_4	7.9	20.5	6.7	7.9		
31	CF	4.2	14.7		6.6		
32	CHF	12.0	7.3				
39	C_3H_3	2.9	6.0	6.1	5.4	6.0	
51	CHF_2	6.6		3.6	3.3		
59	C_3H_4F	5.3		5.9	4.3	6.0	
64	$C_2H_2F_2$	32.7	30.0	48.3	44.7	49.7	84.2
77	$C_3H_3F_2$	2.6		7.8	5.0	7.8	2.1[e]
89	$C_4H_3F_2$	5.3		7.6	5.4	8.3	1.5
100	C_2F_4	7.5	5.1	7.4	5.8	9.9	7.9
109	$C_4H_4F_3$	2.9		6.6	5.1	12.2	1.2[e]

113	C_3HF_4	0.1			0.9[e]
128	$C_4H_4F_4$	0.1		1.0	1.5
192	$C_6H_6F_6$		0.1		0.7

[a]All intensities are mass corrected and normalized to the total intensity of 100. Some minor ions not shown in the table.

[b]From Chapter I.

[c]Taken from delay time experiments. Mass correction is proportional to the inverse square root of the mass.

[d]Mass correction is proportional to the reciprocal mass.

[e]Seen by Jennings et al., Reference 13.

From the fragmentation pattern shown in Table V it is clear that the behavior of the stable molecule $c-C_4H_4F_4$ under electron impact is very similar to that of the ion-molecule collision complex (as shown in Chapter I).

Under conditions of elevated pressure, long residence time, or both, the primary fragments from tetrafluorocyclobutane are available to enter into subsequent ion-molecule reactions with substrate. The abundance of the parent ion is so low, however, that it cannot make a significant contribution to the observed ion-molecule reactions. Several of the C_1 species are of moderate abundance (ca. 6 to 12%); they react so rapidly with substrate that is difficult to ascertain the details of the processes involved. It appears likely (Figures (4) and (5)) that they form one or more of the ethylenic ions. It can be seen in Figures (4), (5), and (6) that the predominant reactions at intermediate pressures and/or residence times involve formation and decay of the ethylenic ions $C_2H_4^+$, $C_2H_2F_2^+$, and $C_2F_4^+$.

The changes in the abundance of the major ions at low pressures due to increases in pressure or residence time are shown in Table V. At lower pressures (of the order of 27 microns) and short delay times, the ions heavier than $C_2F_4^+$ are absent. When the delay time is increased the heavier ions increase in abundance. At higher pressures (of the order of 50 microns), all the ions seen at lower pressures are present throughout the range of delay times studied, including the heavy ions which at 27 microns were seen only at long

delay time. As seen in the table, the intensities of $C_2H_2F_2^+$, $C_2F_4^+$, and $C_4H_4F_3^+$ increase with increases in both the pressure and delay time, while $C_2H_4^+$ and CF^+ abundancies decrease. The same trend continues at higher pressures, as shown by the ICR spectrum. (Even though the pressure in the ICR mass spectrometer was lower than in the Bendix mass spectrometer, the very long residence times in the former instrument allow for a large number of collisions before the ions are lost to the walls or removed from the cell.) This result clearly shows that $C_2H_2F_2^+$ is the major ion in this system at higher pressures (for example, pressures of 10 to 50 Torr in radiolysis experiments).

Although $C_2H_2F_2^+$ was found to react with the substrate, the rate constant for the process must be quite small. In experiments using the Bendix T-O-F, the $C_2H_2F_2^+$ ion was the most abundant even at high pressures and long delay times. The low reactivity of $C_2H_2F_2^+$ is substantiated by the experiments using ICR, where mass corrected ion intensity fraction of this ion was measured as a function of pressure (from 1 x 10^{-6} to 1 x 10^{-4} Torr). There was no measurable change in intensity of the ion with the change in pressure.

In contrast, $C_2H_4^+$ is a very reactive ion. The intensity of $C_2H_4^+$ decays to zero within a few microseconds with the concomitant increase in the intensity of $C_2H_2F_2^+$ (Figures (4) and (5)). The same is true in the pressure dependence experiments where the growth of $C_2H_2F_2^+$ accompanied the decay of $C_2H_4^+$ with increasing pressure (Figure (6)).

The reaction leading to the decay of $C_2H_4^+$ could be a charge transfer from $C_2H_4^+$ to $c\text{-}C_4H_4F_4$, followed by the decomposition of the $C_4H_4F_4^+$ intermediate to give $C_2H_2F_2^+$.

$$C_2H_4^+ + c\text{-}C_4H_4F_4 \longrightarrow C_4H_4F_4^+ + C_2H_4 \qquad \text{II.(2a)}$$

$$C_4H_4F_4^+ \longrightarrow C_2H_2F_2^+ + C_2H_2F_2 \qquad \text{II.(2b)}$$
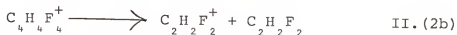
However, this reaction would be thermodynamically unfavorable by 42 kcal, unless $C_2H_4^+$ in Equation II.(2) is in an excited state. Hence, it is to be concluded that $C_2H_4^+$ reacts with $C_4H_4F_4^+$ to give $C_2H_2F_2^+$ and $C_4H_6F_2$, the product $C_4H_6F_2$ having a heat of formation of at least -108 kcal/mole. A heat of formation of -108 kcal/mole is a reasonable value to be expected for a C_4 compound.

$$C_2H_4^+ + c\text{-}C_4H_4F_4 \longrightarrow (C_6H_8F_4^+)^* \longrightarrow C_2H_2F_2^+$$
$$+ C_4H_6F_2 \qquad \text{II.(3)}$$
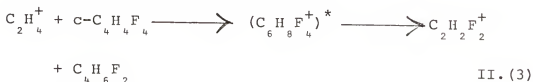
Reaction II.(3) could proceed through either a six center intermediate or attack of $C_2H_4^+$ on a C-C σ bond in $c\text{-}C_4H_4F_4$. There is considerable evidence for the reaction of carbocation on a C-C σ bond, as presented by Olah,[38] whereas a six center complex has not been established. Accordingly, we expect Reaction II.(3) to be a simple radical ion ($C_2H_4^+$) attack on the C-C σ bond connecting two methylene groups in $c\text{-}C_4H_4F_4$, followed by the rupture of the C_6 ion to give $C_2H_2F_2^+$. Since the reaction occurs in the gas phase, the energy-rich C_6 intermediate would tend to decompose, unlike

the situation in Olah's "magic acid" solvents, where the intermediate undergoes collision deactivation followed by atom migration to give a stable product. Several intermediates and ultimate products are probable, depending on which of the different C-C bond types is attacked, and how the transient C_6 ion ruptures. However, attack on the most electron-rich of the three bond types ($-CH_2--CH_2-$) would lead to formation of the most abundant product $C_2H_2F_2^+$ while attack at the next richest site ($-CF_2--CH_2-$) would explain a small production of C_2F_4.

Although the agreement is only moderate, the rate constant for the disappearance of $C_2H_4^+$ in Table IV can be equated to the sum of rate constants for formation of $C_2H_2F_2^+$ and $C_2F_4^+$. It will be seen that the sum of the two formation rate constants is somewhat smaller than the $C_2H_4^+$ decay rate constant at 27 microns, and considerably smaller at 53 microns. We suggest that this discrepancy is due to a reaction in which $C_2H_2F_2^+$ is lost by reaction with substrate; several products are possible including $C_4H_4F_3^+$, which would be formed by a fluoride ion transfer process.

$$C_2H_2F_2^+ + c-C_4H_4F_4 \longrightarrow C_2H_2F_3 \cdot + C_4H_4F_3^+ \qquad II.(4)$$
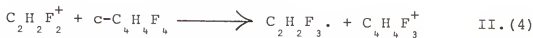
As predicted by this model, the discrepancy between k_{loss} ($C_2H_4^+$) and $k_{formation}$ ($C_2H_2F_2^+ + C_2F_4^+$) increases with an increase in pressure. The reactions of $C_2H_4^+$ mentioned above could not be established using ICDR since the intensity of $C_2F_4^+$ was very small.

The small abundance of species heavier than 128 (the parent) shows the relative unimportance of ion-molecule condensation reactions in this system. Of the three heavy ions (m/e 142, 164, and 192), only the one at 192 was seen both in the Bendix and ICR. The relatively small intensity of this ion forbade any kind of time or pressure dependence measurements. However, using the ICDR technique we could show that at least one of the routes of formation is by the reaction of $C_2H_2F_2^+$ with c-$C_4H_4F_4$. As mentioned in the Results section, this ion is formed by an exoergic reaction.

$$C_2H_2F_2 + c\text{-}C_4H_4F_4 \longrightarrow C_6H_6F_6^+ \qquad \text{II.(5)}$$

$$m/e = 64 \quad m/e = 128 \qquad m/e = 192$$

The ion of mass 142 was seen only in the ICR and the one at 164 only in the Bendix. Again, the intensities of these ions were very small indicating small rate constants for the formation of these products. The ion at mass 142 ($C_5H_6F_4^+$) was also formed by the reaction of $C_2H_2F_2^+$ with c-$C_4H_4F_4$ as shown by ICDR.

$$C_2H_2F_2^+ + c\text{-}C_4H_4F_4 \longrightarrow C_5H_6F_4^+ + CF_2 \qquad \text{II.(6)}$$

$$m/e = 64 \quad m/e = 128 \qquad m/e = 142 \quad m/e = 50$$

Again, this ion ($C_5H_6F_4^+$) is formed through an exoergic reaction. This observation is compatible with the absence of this ion in the Bendix experiments where the electron energy was 100 eV, which would tend to increase the energy

of the reactant ion, $C_2H_2F_2^+$.

The route for the formation of the ion at mass 164 ($C_4H_2F_6^+$) was not established because this ion was absent in the ICR. However, it is very likely that $C_2H_2F_2^+$ is responsible for this ion also. The occurrence of $C_4H_2F_6^+$ in the Bendix and not in the ICR suggests that the lifetime of the ion is very small, perhaps of the order of 2 μsec or less.

CHAPTER III

THE Hg6($^3P_1$) PHOTOSENSITIZED DECOMPOSITION
OF 1,1,2,2-TETRAFLUOROCYCLOBUTANE

Introduction

Mercury 6($^3P_1$) photosensitized decomposition studies on
a large number of alkanes and cycloalkanes have established
that C-H bond rupture is the primary quenching process in
these systems.[39,40] Work on a few partially fluorinated
hydrocarbons has indicated that in these systems as well,
C-H bond scission is the primary mode of quenching the ex-
cited mercury.[41] Only a limited amount of work has appeared
dealing with mercury sensitized decomposition of perfluoro-
carbons (whether open chain or cyclic); details of the de-
composition mechanism have not been established.[4] There have
been no previously reported investigations of the mercury
sensitized decomposition of partially fluorinated cyclobutanes
or other cycloalkanes.

The present investigation of the mercury sensitized
photolysis of 1,1,2,2-tetrafluorocyclobutane was undertaken
in parallel with studies of the gamma radiolysis, mass spec-
trometric fragmentation, and ion-molecule reactions of this
compound. It was expected that mechanistic information derived
from the photolytic (and mass spectrometric) studies would aid

in interpretation of the more complex radiolytic system.

Experimental Section

Sample Preparation

The vessel used in photolysis experiments had a volume of 91 cc; it was constructed of 18 mm ID GE type 204 clear fused quartz and was equipped with a glass break seal and side arm (Figure (7)). To clean the vessel between experiments, it was soaked in nitric acid overnight to remove inorganic material (especially mercury), rinsed with distilled water, and annealed at 565° C to pyrolyze any organic materials on the walls. Before introducing the sample a drop of triple-distilled mercury was placed in the vessel, and the vessel pumped on for at least six hours. In the case of photolysis of the pure system, samples of $c\text{-}C_4H_4F_4$ were measured in a standard volume using PVT technique, transferred to the photolysis vessel, and sealed under vacuum. For photolysis of a mixture of hydrogen and $c\text{-}C_4H_4F_4$, the tetrafluorocyclobutane was introduced as above, the photolysis vessel immersed in liquid nitrogen, and hydrogen metered directly into the photolysis vessel. After the introduction of hydrogen, the vessel was very cautiously sealed. The pressure of hydrogen in the vessel at room temperature (297° K) would be 3.87 (i.e., 297° K/77° K) times the measured pressure. For quenching cross section and actinometry experiments, $c\text{-}C_4H_4F_4$ was introduced as in the case of the pure system; a premeasured amount of N_2O from a standard vessel was vacuum
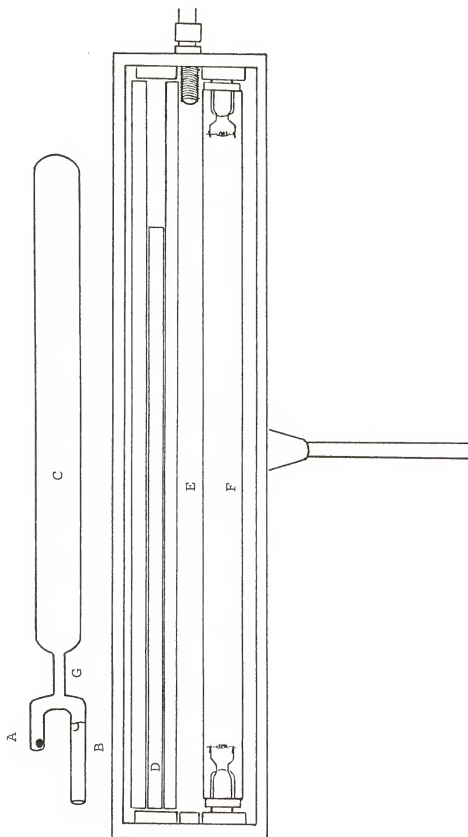
Figure 7. The photolysis set up: A, mercury drop; B, break seal; C, reaction cell; D, glass tube to support the photolysis vessel; E, desk lamp fixture; F, germicidal lamp; G, graded seal.

transferred into the photolysis vessel and sealed under vacuum. The purification of $c\text{-}C_4H_4F_4$ has been described in Chapter IV. N_2O obtained from Matheson Gas Company was subjected to at least ten freeze-pump-thaw cycles to remove air before use; C.P. grade Matheson H_2 was used as received.

Sample Irradiation

To maintain a constant mercury vapor pressure in mercury sensitization experiments, it is common to provide a small drop of liquid mercury in direct contact with the vapor phase. To obtain reproducible results, however, we found it necessary to make sure that the drop was in a small side arm, and not in the main reaction cell exposed to the full lamp intensity.

The source of 253.7 nm light was a General Electric 15 W Germicidal lamp (type G15T8) which is essentially a low pressure mercury lamp in a high silica envelope, which transmits 253.7 nm and not 184.9 nm (Figure (7)). This lamp was mounted inside a standard desk lamp fixture equipped to hold two fluorescent tubes. The second lamp was replaced by a stack of Pyrex tubes which provided reproducible positioning of the sample vessel. To avoid intensity variations due to AC line voltage fluctuations, a Sola saturable core transformer was used to power the lamp. The photolysis arrangement was covered with a wooden eye shield and air was blown through this set-up to remove any ozone formed and to keep the temperature constant. The temperature was recorded using a

thermometer with its bulb resting inside the photolysis
cavity. This experimental arrangement is essentially the
same as the one described in detail by Dr. Arthur J. Frank
of this laboratory.[42] After photolysis, the sample was
cooled down to liquid nitrogen temperature to prevent any
dark reactions.

Product Identification and Analysis

The organic product identification was done using an
on-line gas chromatograph-mass spectrometer combination.
Hydrogen was measured by the conventional Toepler pump -
McLeod gauge arrangement and the organic products by flame
ionization gas chromatography. The details of identification
and analyses are given in Chapter IV and Appendix I.

Preparatory to a wet-chemical analysis of HF, an extrac-
tant solution of 2 ml of 66% ethanol in water was introduced
into the tubulation extending beyond the break-seal on the
photolysis vessel (Figure (7)). With the cell contents
frozen, the break seal was opened with a rod introduced
through a piece of rubber tubing used as a gland. This pro-
cedure was necessary to avoid condensation of oxygen inside
the vessel. The vessel was warmed to room temperature and
the ethanolic solution was left in contact with the walls of
the vessel for at least 30 minutes to extract all the fluoride
ion into the solvent. This solution was transferred into a 5
ml polyethylene beaker, and the vessel was rinsed out into the
beaker with another 2 ml of 66% ethanol.

The determination of HF was based on a previously described

electrochemical procedure;[43] however, it was necessary to make a minor modification to permit analysis in the presence of mercury or mercuric ions. A drop of dilute aqueous NaCl was added to the fluoride ion solution prepared as described above.

To make sure that the added chloride ion was not interfering with the fluoride ion determination, a series of experiments using known amounts of NaF was carried out. (The Orion fluoride ion selective electrode, model 94-09, used in these experiments is claimed to have a selectivity of 1000:1 over chloride ions.[44]) In these verification experiments 40 μl of 5.00 x 10^{-3}M NaF was titrated against 5.00 x 10^{-3}M La(NO$_3$)$_3$ solution, in the presence of chloride ion and/or mercuric ion and mercury. Figure (8) shows the titration curves for these analyses. In case of the titration in the presence of mercuric ions, the EMF changed from -0.052 V to -0.003 V soon after the addition of mercuric ion indicating the complexation of fluoride ions with mercuric ions; the subsequent addition of chloride ion changed the EMF back to -0.051 V, indicating the release of fluoride ion into the solution. These experiments show that the chloride ions (which can be used to release fluoride ions from mercuric ions and/or mercury) do not interfere with the determination of fluoride ions.

In all these experiments, the procedure prescribed by Heckel[44] was followed. It was essential to condition the fluoride ion selective electrode by performing at least two
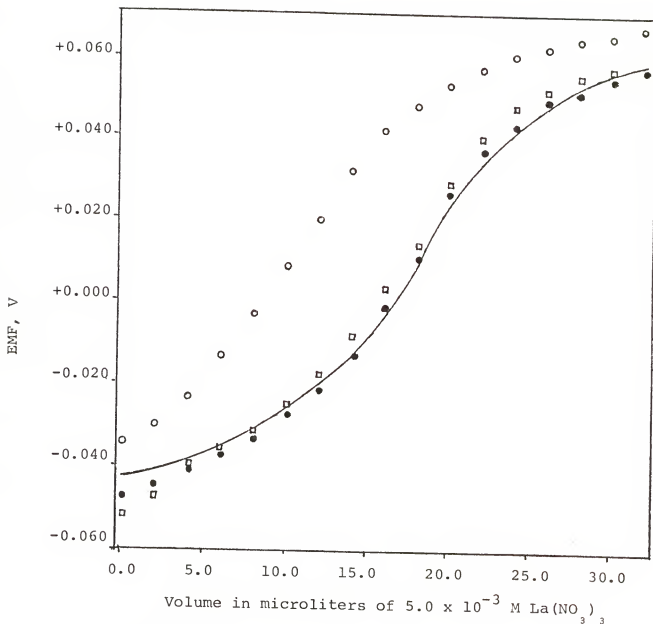
Figure 8.   Titration curves for quantitative analysis of
F$^-$ ion: 40 µl of NaF + HG^{2+} ion + Cl$^-$ ion,   ;
40 µl of NaF + Cl$^-$ ion,   ; 40 µl of NaF, solid
line; photolysis, O.

titrations using this electrode before it could be used for a quantitative determination. During all the titrations, the analyte was continuously stirred using a magnetic stirrer, and the EMF was monitored using a high input impedance (10 Mega Ohm) Hickock digital Volt-Ohm meter.

Nitrogen formed in the photolysis of a mixture of N_2O and c-$C_4H_4F_4$ was transferred from the photolysis vessel immersed in liquid nitrogen via a Toepler pump into a McLeod gauge where it was measured.

Results

Quenching Cross Section Measurements and Actinometry

For quenching cross section measurements and actinometry four mixtures with different pressure ratios of c-$C_4H_4F_4$ to N_2O ($P_{c-C_4H_4F_4}/P_{N_2O}$) were photolysed for 30 sec. In each sample, the total pressure was 50 Torr. A plot of the reciprocal of the number of moles of nitrogen formed in each mixture against the quantity ($P_{c-C_4H_4F_4}/P_{N_2O}$) gave a straight line as shown in Figure (9). The intercept of this line gives the reciprocal of the number of moles of nitrogen formed in pure N_2O. The amount of nitrogen formed in the absence of c-$C_4H_4F_4$ was found to be 9.597 μmoles. Assuming a quantum yield of 0.8 for N_2 production in mercury sensitized photolysis of N_2O,[40] the absorbed light intensity was calculated to be 2.4×10^{17} quanta/sec in the 91 cc vessel (i.e., 24 μEinsteins/min). The quenching cross section of c-$C_4H_4F_4$ was determined relative to that of nitrous oxide.[40] The
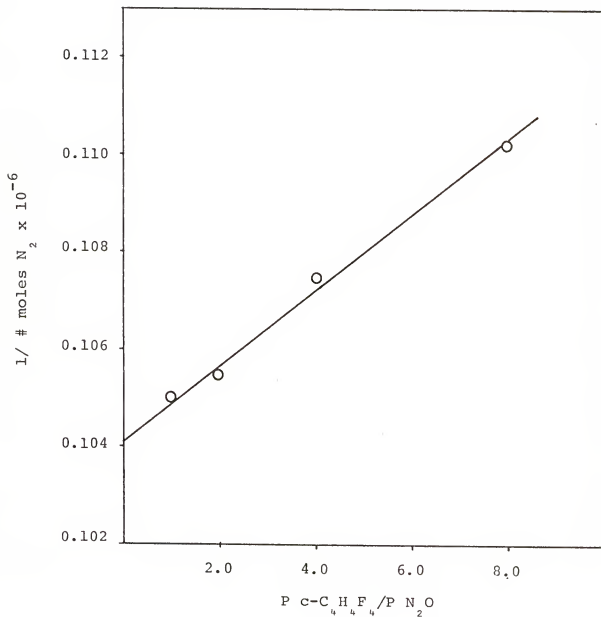
Figure 9. Modified Stern-Volmer plot; a plot of the reciprocal of the number of moles of N_2 against the ratio of the pressure of $c-C_4H_4F_4$ to that of N_2O.

ratio, β, of the relative quenching rates for c-$C_4H_4F_4$ and nitrous oxide was calculated from the slope of the line in Figure (9) to be

β = (slope) x (number of photons absorbed in 30 sec)/
      Avagadro's number

β = 0.0102

The quenching cross section of c-$C_4H_4F_4$ was calculated using the equation[40]

$$\frac{\sigma^2_{c\text{-}C_4H_4F_4}}{\sigma^2_{N_2O}} = \beta \left[\frac{1 + (M_{Hg}/M_{N_2O})}{1 + (M_{Hg}/M_{c\text{-}C_4H_4F_4})}\right]^{\frac{1}{2}}$$

where σ^2 is the quenching cross section and M is the molecular weight of the species shown by the subscripts. Assuming the quenching cross section of N_2O determined by the chemical method to be 18 $\overset{o}{A}{}^2$ (Reference (40)), $\sigma^2_{c\text{-}C_4H_4F_4}$ is calculated to be 0.27 $\overset{o}{A}{}^2$. Recently Gleditsch and Michael[45] have given a value of 22.1 $\overset{o}{A}{}^2$ as the preferred value for $\sigma^2_{N_2O}$. Using this value of $\sigma^2_{N_2O}$, the corresponding value of $\sigma^2_{c\text{-}C_4H_4F_4}$ is 0.31 $\overset{o}{A}{}^2$.

Photolysis Products

The major products formed in the photolysis of c-$C_4H_4F_4$ at 50 Torr are HF, C_2H_6, $C_3F_4H_2$, two isomers of $C_6H_4F_6$ (hereafter referred to as $C_6H_4F_6$ (I) and $C_6H_4F_6$ (II)), an unidentified C_8 compound, and $C_8H_6F_8$ (a bicyclic compound); the minor products were H_2, CH_4, C_2F_4, 1,1- difluoroethylene (1,1-$C_2H_2F_2$)

and C_2F_3H. There were at least two more products whose
yields were not recorded since they were formed in very
small quantities and their compositions were unknown. Based
upon the ^{19}F NMR and mass spectral cracking pattern the
probable structure of $C_6H_4F_6$ (I) is as follows:

```
          H   H   F    F
          |   |   |    |
     H — C — C — C  =  C
          |   |   |     \
     F — C — C — F       H
          |   |
          F   F
```
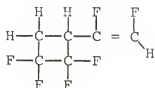
The other isomer, $C_6H_4F_6$ (II), is probably non-cyclic as
indicated by its proton NMR. We could determine neither
the structure nor the exact composition of the C_8 compound.
Further discussions of the composition and structure of some
of the photolysis products are given in Chapter IV and
Appendix II.

A series of experiments was performed to investigate
the dependence of product yields on photolysis time in pure
1,1,2,2-tetrafluorocyclobutane. These experiments were
carried out at both 50 and 150 Torr of the tetrafluorocyclo-
butane to reveal a possible pressure effect. The yields of
C_2H_6 and two isomers of $C_6H_4F_6$ increased linearly with
irradiation time. The rest of the products were formed at
a decreasing rate at longer irradiation times and many of
the yields approached limiting values after two minutes of
photolysis. Figures (10) - (14) show the yield-photolysis
time plots for all products at both pressures. Quantum
yields for all products at 120 sec photolysis time for a 50
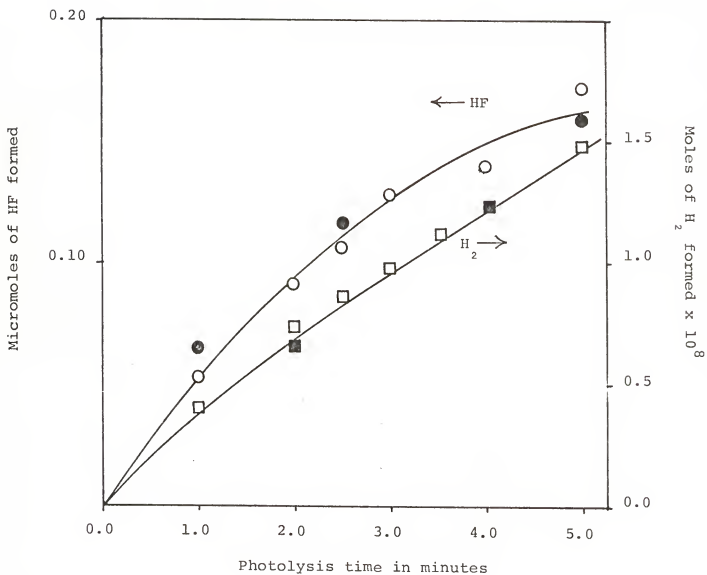
Figure 10. Yield of HF (○ at 50 Torr; ● at 150 Torr) and H_2 (□ at 50 Torr; ■ at 150 Torr) as a function of time in the photolysis of $c\text{-}C_4H_4F_4$.
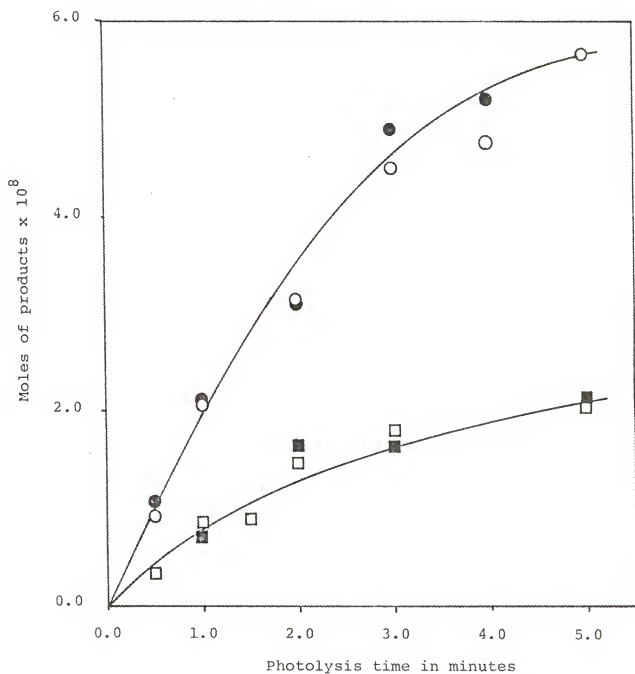
Figure 11. Yield of $C_3H_2F_4$ ($\bigcirc$ at 50 Torr; $\bullet$ at 150 Torr) and C_2HF_3 ($\square$ at 50 Torr; $\blacksquare$ at 150 Torr) as a function of time in the photolysis of $c\text{-}C_4H_4F_6$.
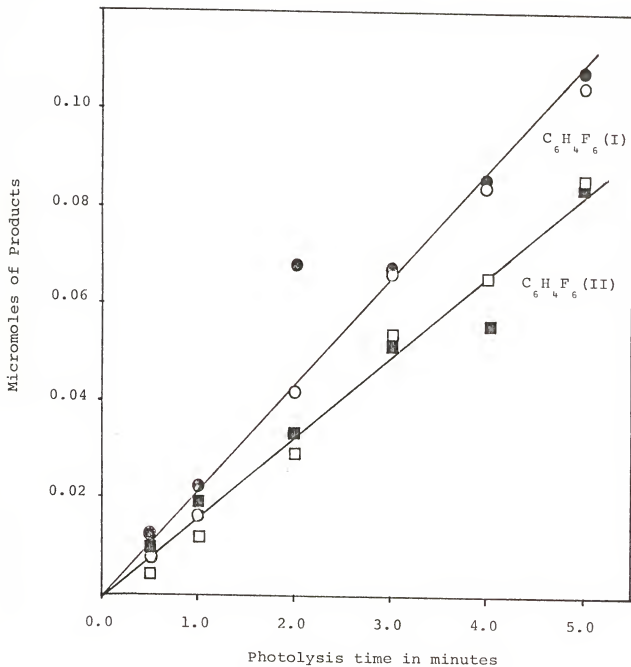
Figure 12. Yield of $C_6H_4F_6$(I) ($\bigcirc$ at 50 Torr; $\bullet$ at 150 Torr) and $C_6H_4F_6$(II) ($\square$ at 50 Torr; $\blacksquare$ at 150 Torr) as a function of time in the photolysis of c-$C_4H_4F_4$
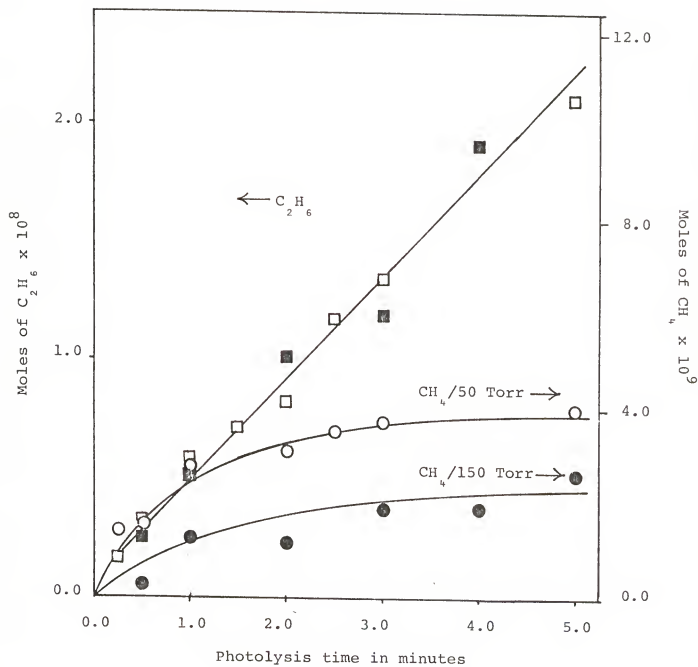
Figure 13. Yield of C_2H_6 ($\square$ at 50 Torr; $\blacksquare$ at 150 Torr) and CH_4 ($\bigcirc$ at 50 Torr; $\bullet$ at 150 Torr) as a function of time in the photolysis of $c\text{-}C_4H_4F_4$
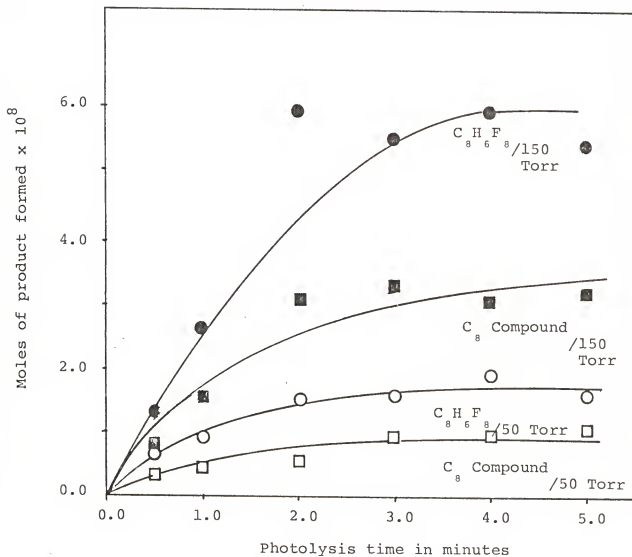
Figure 14. Yield of $C_8H_6F_8$ (O at 50 Torr; ● at 150 Torr) and the C_8 compound (□ at 50 Torr; ■ at 150 Torr) as a function of photolysis time.

Torr sample are shown in Table VI. Since the absolute yields are quite small, a set of relative yield values normalized to HF yield = 1.00 are also given in the Table, in order to give a clearer picture of the behaviors of the system.

Since the yields of CH_4, the C_8 compound and $C_8H_6F_8$ at 150 Torr were different from those at 50 Torr, a series of 120 sec irradiations were carried out using pure $c-C_4H_4F_4$ at three more pressures ranging from 10 to 150 Torr. Yields of all the products except CH_4, the C_8 compound and $C_8H_6F_8$ were independent of pressure above 30 Torr, within experimental error. The yields of methane decreased with increase in pressure while those of the C_8 compound and $C_8H_6F_8$ increased linearly as shown in Figure (15).

To establish whether any of the products were due to the reactions of hydrogen atoms, a mixture of 400 Torr of H_2 and 20 Torr of $c-C_4H_4F_4$ was photolysed for 300 sec. All the products formed in the pure system were formed except C_2F_4, $C_6H_4F_6$ (II), the C_8 compound and $C_8H_6F_8$. The yields of products formed in this experiment are given in Table VII.

The material balance in the photolysis is reasonably good. The ratio of C/H/F is 4.00/3.65/4.48 when the photolysis has progressed for 120 sec. This shows a shortage of carbon and hydrogen. However, at shorter photolysis times the material balance is better, and at longer photolysis times worse. This suggests the formation of polymers or products which were not analyzable by the methods used in these experiments.

TABLE VI

Yields of Products Formed in a 120 Sec
Photolysis of 50 Torr of $c\text{-}C_4H_4F_4$

Product	Yield at 120 sec in μ moles	Quantum Yield	Relative Yield
HF	0.091	0.0019	1.0
H_2	0.006	0.00012	0.063
CH_4	0.0016	0.00003	0.016
C_2H_6	0.0095	0.000197	0.10
C_2F_4	0.0015	0.00003	0.016
$C_2H_2F_2$	0.00092	0.00002	0.010
C_2HF_3	0.00161	0.000033	0.017
$c\text{-}C_3H_2F_4$	0.0310	0.0006	0.34
$C_6H_4F_6$ (I)	0.046	0.000954	0.50
$C_6H_4F_6$ (II)	0.031	0.000643	0.34
C_8 ?	0.009	0.000186	0.10
$C_8H_6F_8$	0.020	0.00041	0.22
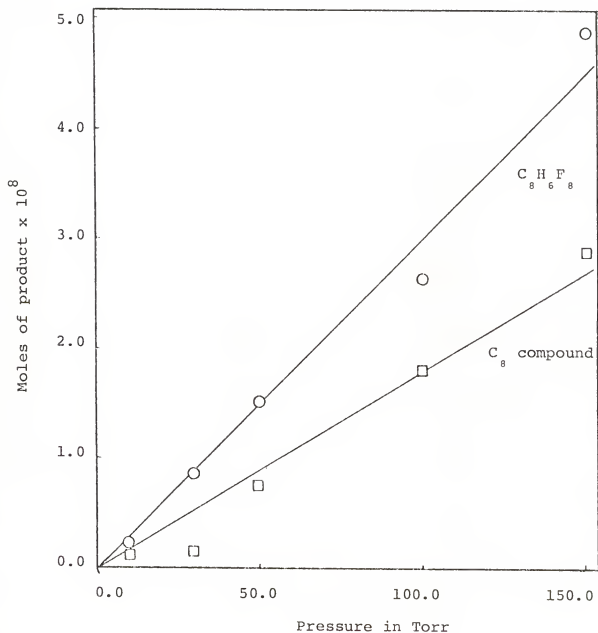
Figure 15. Plots of yields of $C_8H_6F_8$ (O) and the C_8 compound (□) as a function of pressure in the photolysis vessel.

TABLE VII

Yields of Products Formed in a 300 Sec Photolysis
of a Mixture of 400 Torr of H_2 and 20 Torr of c-$C_4H_4F_4$

Product	Amount in μmoles	Relative Yield
HF	0.2348	1.0000
CH_4	0.0019	0.0082
C_2H_6	0.0125	0.0530
$C_2H_2F_2$	0.0021	0.0090
C_2HF_3	0.0308	0.1310
c-$C_3H_2F_4$	0.0025	0.0106
$C_6H_4F_6$ (I)	0.0019	0.0082

Discussion

The possibility of direct photolysis of $c\text{-}C_4H_4F_4$ by 253.7 nm light can be ignored since $c\text{-}C_4H_4F_4$ has no absorption above 180.0 nm.[46] Hence, all of the observed products in these experiments must be due to the quenching of $Hg6(^3P_1)$ to the $6(^1S_0)$ ground state by $c\text{-}C_4H_4F_4$. (Although it is possible to quench $Hg6(^3P_1)$ to the $6(^3P_0)$ state, this process has been shown to be unimportant in many systems[47] and we ignore it for lack of any direct evidence.) That $c\text{-}C_4H_4F_4$ is not very efficient in quenching the $Hg6(^3P_1)$ is shown by its relatively small value of 0.3 $\overset{\circ}{A}^2$ for the quenching cross section (based on a value of 18 $\overset{\circ}{A}^2$ for $\sigma^2_{N_2O}$). This inefficiency in quenching is in accordance with the generalization, discussed by Cvetanovic,[40] that cycloalkanes are analogous to alkanes in their low quenching efficiency. A value of 0.3 $\overset{\circ}{A}^2$ for $\sigma^2_{c\text{-}C_4H_4F_4}$ is similar to the reported quenching cross sections of three partially fluorinated alkanes — CH_3CH_2F (0.46 $\overset{\circ}{A}^2$), CH_3CHF_2 (0.45 $\overset{\circ}{A}^2$), and CH_3CF_3 (0.45 $\overset{\circ}{A}^2$).[41] As expected this value for the quenching cross section of $c\text{-}C_4H_4F_4$ is considerably smaller than those of comparable alkanes or cycloalkanes but larger than those of perfluoroalkanes (e.g., $\sigma^2_{c\text{-}C_4H_8} = 6.7 \overset{\circ}{A}^2$ and $\sigma^2_{CF_4} \ll 0.005 \overset{\circ}{A}^2$).[40,47]

The primary photophysical event is shown in Equation III.(1) and the subsequent quenching in Equation III.(2).

$$Hg6(^1S_0) + h\nu \ (253.7 \ nm) \longrightarrow Hg6(^3P_1) \qquad III.(1)$$

$$\text{Hg6}(^3P_1) + c\text{-}C_4H_4F_4 \longrightarrow C_4H_3F_4 \cdot + H \cdot + \text{Hg6}(^1S_0)$$
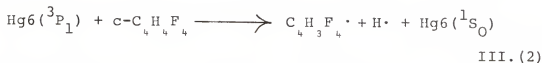
III.(2)

It is suggested that the quenching of $\text{Hg6}(^3P_1)$ by $c\text{-}C_4H_4F_4$ leads to the scission of a C-H bond (Reaction III.(2)). Rupture of the C-C bond is not suggested since we saw no evidence for it. Reaction III.(2) is suggested to be the major quenching process because of the following three reasons: (a) C-H bond rupture has been established to be a major quenching process in cycloalkanes;[3,40] (b) the products formed in photolysis of pure $c\text{-}C_4H_4F_4$ and those in a mixture of a large amount of hydrogen and a small amount of $c\text{-}C_4H_4F_4$ are similar, suggesting that hydrogen atoms are formed in the quenching process in this system; and (c) when a mixture of $c\text{-}C_4H_4F_4$ and I_2 was photolysed in the presence of mercury vapor, all the products in the photolysis were eliminated, and a new product identified as $C_4H_3F_4I$ (on the basis of GC retention time and the mass spectral fragmentation pattern) was formed. These three observations argue very heavily in favor of Reaction III.(2) as the primary quenching process.

The two radicals $C_4H_3F_4 \cdot$ and $H \cdot$ (formed in the primary process) can react with each other or with the substrate gas leading to the formation of the observed photolysis products. We were able to study the simple reactions resulting from reactions of $H \cdot$ and fluorobutyl radicals in the absence of the more complex reactions resulting from mutual reactions of fluorobutyl radicals by photolyzing a mixture of H_2 and $c\text{-}C_4H_4F_4$ in the presence of mercury vapor. These experiments

are discussed first, followed by consideration of the more
complex pure system.

In the photolysis of a mixture of 400 Torr of hydrogen
and 20 Torr of $c-C_4H_4F_4$, essentially all the excited mercury
atoms will be quenched by hydrogen since its quenching cross
section ($8.6 \overset{o}{A}^2$)[47] and relative amount are each twenty times
larger than those of $c-C_4H_4F_4$; thus only about one quenching
event in 400 will involve the fluorocarbon directly.

$$Hg6(^3P_1) + H_2 \longrightarrow 2H\cdot + Hg6(^1S_0) \qquad \text{III.(3)}$$
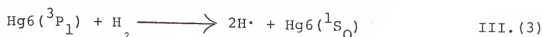
It is possible that this reaction proceeds via formation of
HgH, although leading to the same final products. Since $H\cdot$
would be the only reactive species formed in the quenching
process, all the products seen in the mixture of H_2 and
$c-C_4H_4F_4$ must be due to the reactions of $H\cdot$ with $c-C_4H_4F_4$.
Expected reaction of hydrogen atoms would be either an ab-
straction of $H\cdot$ from the substrate or an addition to substrate
with simultaneous ring opening.

$$H\cdot + c-C_4H_4F_4 \longrightarrow H_2 + c-C_4H_3F_4\cdot \qquad \text{III.(4)}$$

$$H\cdot + c-C_4H_4F_4 \longrightarrow (CH_3CH_2CF_2CF_2\cdot)* \qquad \text{III.(5)}$$
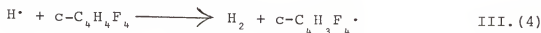
Production of $H\cdot$ in Reaction III.(4) can not be observed
directly due to the presence of excess hydrogen. However,
results from the pure system discussed below suggest that
Reaction III.(4) is considerably less efficient than Reaction
III.(5).

We have postulated the addition of hydrogen atom to a carbon bonded to hydrogen, since in 1,1-difluoroethylene hydrogen atoms add almost exclusively at the nonfluorinated carbon end of the molecule,[48] indicating that the addition to the methylene group is more favorable than to the perfluoromethylene group. Furthermore, the radical site in the product of Reaction III.(6) is expected to be the terminal CF_2 group, since fluorine atoms are known to stabilize radicals.[49]

Extended considerations of the observed product distribution requires that we postulate a substantial contribution from a third hydrogen atom reaction, namely abstraction of a fluorine atom from substrate.

$$H\cdot + c\text{-}C_4H_4F_4 \longrightarrow HF + c\text{-}C_4H_4F_3\cdot \qquad \text{III.(6)}$$
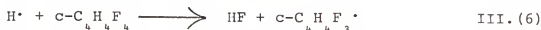
Although such a reaction is thermodynamically favorable in most cases, it is generally not observed, presumably due to unfavorable kinetic factors. The reaction should be especially favorable in a cyclobutane; however, the near - $90°$ ring angles prevent good sp^3 hybridization, decreasing sigma bond energies, and enhance accessibility of both the carbon atom and substituents to attack.

The fates of the three radicals, $c\text{-}C_4H_3F_4\cdot$, $(CH_3CH_2CF_2CF_2\cdot)*$ and $c\text{-}C_4H_4F_3\cdot$ (formed in Reactions III.(4) through III.(6)) determine the products formed and their relative distribution observed in the mixture. Since Reaction III.(5) involves formation of a primary C-H bond (ca. 98 kcal/mole[17]) and rupture of a weak C-C bond (61 kcal/mole according to our

measurements) , the product radical will be excited by
approximately 37 kcal, probably mostly in the form of
vibrational energy. This amount of energy is easily
sufficient to cause HF elimination, which is not more than
15 kcal endoergic:

$$(H_3CCH_2CF_2CF_2\cdot)^* \longrightarrow HF + CH_3CH = CFCF_2\cdot$$

<div align="right">III.(7)</div>

The reaction probability is further enhanced by the fact
that the product is a relatively stable vinyl radical.
Reaction III.(7) would occur in competition with thermali-
zation of the precursor species and we expect that it is a
moderately important process.

The final fate of the radicals in Reaction III.(7) should
be reaction with hydrogen atoms, which are present in much
larger concentration than any other radicals in the system.
The product ($CH_3CH = CFCF_2H$) would initially contain excess
energy due to C-H bond formation which could either lead to
further fragmentation or be lost in thermalizing collisions.
Although no product having the formula $CH_3CHCFCF_2H$ was observed,
it might easily be masked by elution with the parent c-$C_4H_4F_4$.
Since the measured product yields indicate a surplus of
fluorine relative to carbon and hydrogen, formation of a
moderate amount of this compound would improve the material
balance.

The decomposition of ($CH_3CH_2CF_2CF_2\cdot$)* to give either a
methyl or ethyl group is thermodynamically unfavorable

(endoergic by at least 30 kcal/mole for methyl radical formation and 21 kcal/mole for ethyl radical elimination). However, the product of H· and $CH_3CH_2CF_2CF_2$· (either excited or collisionally stabilized) certainly contains sufficient energy to undergo decomposition.

$$CH_3CH_2CF_2CF_2· + H· \longrightarrow (CH_3CH_2CF_2CF_2H)^* \qquad \text{III.(8)}$$

$$(H_3CCH_2CF_2CF_2H)^* \longrightarrow CH_4 + c\text{-}C_3H_2F_4 \qquad \text{III.(9)}$$

$$(CH_3CH_2CF_2CF_2H)^* \longrightarrow C_2H_5· + C_2F_4H· \qquad \text{III.(10)}$$
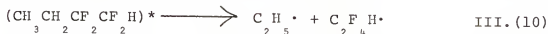
Reactions III.(9) and III.(10) are very similar to those reported for the pyrolytic decomposition of n-butane.[50]

$$n\text{-}C_4H_{10} \longrightarrow CH_4 + C_3H_6 \qquad \text{III.(11)}$$

and

$$n\text{-}C_4H_{10} \longrightarrow 2C_2H_5· \qquad \text{III.(12)}$$

Although the present work was done at room temperature, the energy made available by Reaction III.(8) should be sufficient to drive either Reaction III.(9) or Reaction III.(10). Since Reaction III.(9) involves rupture of a C-C bond (83 kcal) and formation of a C-H bond (102 kcal) and a new C-C bond, the overall process is energetically very favorable. (If the heavier product in Reaction III.(9) is an open chain olefin, the second link in a C=C bond will be formed with an energy release of 63 kcal.)[17] The amount of CH_4 formed is almost equal to that of $C_3H_2F_4$ as expected according to Reaction III.(9). The sequence of Reactions III.(8), III.(10) is

exothermic only to the extent that the C-H bond energy (ca. 98 kcal/mole) exceeds the energy of the C-C bond (83 kcal/mole). Nevertheless, both types of reactions are well established under high temperature conditions[50] and appear plausible here as well.

The fate of $C_2F_4H\cdot$ (from Reaction III.(10)) should be reaction with $H\cdot$, the most abundant radical in the mixture.

$$C_2F_4H\cdot \ + \ H\cdot \ \longrightarrow \ (C_2F_4H_2)* \qquad\qquad III.(13)$$
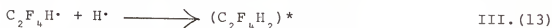
This energy rich ethane molecule could readily undergo HF elimination leading to the formation of C_2F_3H and HF:

$$(C_2F_4H_2)* \ \longrightarrow \ C_2F_3H \ + \ HF \qquad\qquad III.(14)$$

Having considered in some detail the fate of the open chain butyl radical formed in Reaction III.(5), it is now necessary to consider further reactions of cyclic butyl radicals formed by hydrogen and fluorine abstractions (Reactions III.(4) and III.(6), respectively). In the presence of $H\cdot$ as the major steady-state species, the primary fate of $c\text{-}C_4H_3F_4\cdot$ and $c\text{-}C_4H_4F_3\cdot$ should be combination, frequently followed by decomposition of the energy rich cyclobutanes.

$$c\text{-}C_4H_3F_4\cdot \ + \ H\cdot \longrightarrow (c\text{-}C_4H_4F_4)* \longrightarrow
\begin{cases}
C_4H_3F_3 \ + \ HF & III.(15a) \\[6pt]
2C_2H_2F_2 & III.(15b) \\[6pt]
\xrightarrow{M} \ c\text{-}C_4H_4F_4 & III.(15c)
\end{cases}$$

$$\text{c-C}_4\text{H}_4\text{F}_3 \cdot \; + \; \text{H} \cdot \longrightarrow \begin{pmatrix} \text{H} & \text{H} \\ \text{HC} & \text{—CF} \\ \text{HC} & \text{—CF} \\ \text{F} & \text{F} \end{pmatrix}^* \longrightarrow$$

$$\longrightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{HF}_3 \qquad \text{III.(16a)}$$

$$\longrightarrow \text{C}_2\text{H}_2\text{F}_2 + \text{C}_2\text{H}_3\text{F} \qquad \text{III.(16b)}$$

$$\xrightarrow{\text{M}} \text{c-C}_4\text{H}_5\text{F}_3 \qquad \text{III.(16c)}$$
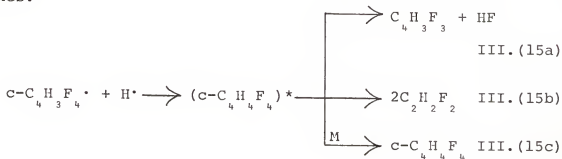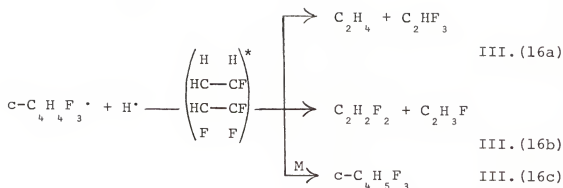
The relative probabilities of the above six reactions are hard to assess since two of the products ($\text{C}_4\text{H}_3\text{F}_3$ and $\text{C}_4\text{H}_5\text{F}_3$) were not observed (since these would probably elute with the parent $\text{c-C}_4\text{H}_4\text{F}_4$ in the gas chromatograph) and the olefins would be labile under photolytic conditions. However, the relatively large yield of C_2HF_3 indicates that Reaction III.(16a) is efficient. One factor which determines the abundance of products formed through Reactions III.(15) and III.(16) is the amount of precursor radical formed in the mixture. Since the amount of C_2HF_3 formed is relatively large in these experiments the concentration of $\text{c-C}_4\text{H}_4\text{F}_3 \cdot$ must be substantial. Hence, we infer that a substantial fraction of the hydrogen atoms in the system undergo Reaction III.(6). Like all the other olefins in the system, C_2HF_3 can undergo H· atom attack. Although C_2HF_3 may be less reactive than some of the other olefins in the system, at least a portion of it should undergo H· addition followed by HF elimination to give $\text{C}_2\text{HF}_2 \cdot$.

$$\text{C}_2\text{HF}_3 + \text{H} \cdot \longrightarrow \underset{\overset{|}{\text{F}}}{\overset{\overset{\text{F}}{|}}{\cdot\text{C}}} = \underset{\overset{|}{\text{H}}}{\overset{\overset{\text{F}}{|}}{\text{CH}}} \longrightarrow \underset{}{\overset{\overset{\text{F}}{|}}{\cdot\text{C}}} = \underset{\overset{|}{\text{H}}}{\overset{\overset{\text{F}}{|}}{\text{C}}} + \text{HF} \qquad \text{III.(17)}$$
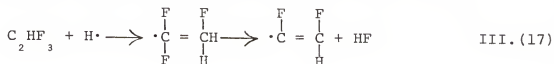
The product $\text{C}_2\text{HF}_2 \cdot$ formed in the above reaction could combine

with any of the radicals in the system. However, we postulate only Reaction III.(18) since $C_6H_4F_6$ (I) is the only such product of combination observed in the mixture.

$$c\text{-}C_4H_3F_4\cdot \; + \; \cdot \underset{\underset{H}{|}}{\overset{\overset{F}{|}}{C}} = \overset{\overset{F}{|}}{C} \longrightarrow C_6H_4F_6 \; (I) \qquad\qquad III.(18)$$
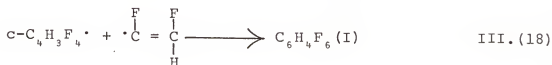
With the above reaction scheme in mind, we proceed with the interpretations of results in the photolysis of pure $c\text{-}C_4H_4F_4$. The major difference between the pure system and the mixture is the relative amounts of the radicals formed. As discussed earlier, $H\cdot$ is the predominant active species in the mixture. However, in the pure system the amount of $H\cdot$ formed initially is equal to that of $C_4H_3F_4\cdot$. Accordingly, most radicals combine with $H\cdot$ in the mixture, whereas in the pure system there is also a substantial probability of radical combination with $c\text{-}C_4H_3F_4\cdot$, leading to considerably greater production of high molecular weight species.

Since $C_4H_3F_4\cdot$ would be the predominant organic radical in the pure system, a combination of two such radicals should be expected.

$$2C_4H_3F_4\cdot \longrightarrow C_8H_6F_8 \qquad\qquad III.(19)$$

This type of addition product of two rings has been observed in the mercury sensitized photolysis of both cyclobutane[3] and perfluorocyclobutane,[4] as well as in the radiolyses of both compounds.[9,10] The $C_8H_6F_8$ in Reaction III.(19) would

certainly be vibrationally excited and might need collisional stabilization.

In addition to $C_8H_6F_8$, another C_8 compound is also formed. Since its composition and structure are not known, it is inappropriate to propose a mechanism for its formation. However, we expect it to be a condensation product of $C_4H_3F_4\cdot$ with one of the many C_4 radicals which are formed.

We propose that $C_6H_4F_6$(I) is formed by the same mechanism in the pure system as in the mixture. The large yield of $C_6H_4F_6$(I) in the pure system is not surprising since it is formed by reaction of $C_4H_3F_4\cdot$ which is present in larger quantities in this case. A second compound with the same empirical formula but (probably) an open chain structure is $C_6H_4F_6$(II). One possible route for its formation would be combination of the $CH_3CH = CFCF_2\cdot$ radical from Reaction III. (7) with $C_2F_3\cdot$, formed by HF elimination from $C_2HF_4\cdot$ subsequent to Reaction III.(10).

It can be noted that the postulated mechanism calls for formation of a variety of olefinic products which were not observed. The olefins would be labile under photolytic conditions, and can undergo polymerization. In fact we did see some white solid on the walls of the vessel when a large amount of $c-C_4H_4F_4$ was photolyzed for a long time. Also, we observed the formation of three products heavier than C_8 compounds at longer irradiation times and higher pressures.

A final point of difference between the pure system and the mixture is the relatively large yield of $C_3H_2F_4$ in the

former case; this is especially noteworthy since no other odd-carbon species is found in nearly as large a yield (34% relative to HF). It appears that a contribution by a route other than Reaction III.(9) is important in the pure system. One such route could be the decomposition of a C_6 compound; two C_6 products are formed with much higher relative yields in the pure system than in the mixtures. A detailed explanation will not be proposed, however, due to lack of further evidence on this point.

In summary, we conclude that $Hg6(^3P_1)$ reacts with c-$C_4H_4F_4$ to cause hydrogen atom production. The resulting free H· atoms react with tetrafluorocyclobutane by hydrogen atom abstraction, fluorine atom abstraction, and addition to the ring (causing ring opening). The radicals formed in these processes combine with each other or with hydrogen atoms; the resulting energy release frequently causes decomposition of the product molecule, such as elimination of HF or rupture of the C_4 ring into two ethylenic compounds. (Radical disproportionation reactions probably also occur but were not specifically identified.) As expected from the postulated mechanism, addition of I_2 scavenger eliminates all products observed in the pure system, and only c-$C_4H_3F_4I$ is detected.

CHAPTER IV

GAMMA-RADIOLYSIS OF 1,1,2,2-TETRAFLUOROCYCLOBUTANE
IN THE GAS PHASE

Introduction

1,1,2,2-tetrafluorocyclobutane differs from both cyclo-
butane and perfluorocyclobutane in many physical and chemical
properties. The thermodynamic stability of tetrafluorocyclo-
butane is between those of c-C_4H_8[51] and c-C_4F_8.[52] Although
there has been a considerable amount of work on the radiolysis
of both c-C_4H_8[8,9] and c-C_4F_8,[10] as well as a study of the
radiolysis of mixtures of the two compounds,[11] there has been
no work reported on a partially fluorinated cyclobutane.
Tetrafluorocyclobutane was chosen for this study for several
reasons, including the fact that it is empirically equivalent
to an equimolar mixture of c-C_4H_8 and c-C_4F_8.

This chapter describes a study of the gas-phase gamma-
radiolysis of pure 1,1,2,2-tetrafluorocyclobutane, including
the effect of added oxygen on the reactions of the system.
To help understand the mechanisms involved in the radiolysis
of this compound, parallel investigations of mercury sensitized
photolysis and ion-molecule reactions in tetrafluorocyclobutane
were also carried out.

Experimental

Reagents

The 1,1,2,2-tetrafluorocyclobutane used in these studies
was obtained from Columbia Organic Chemicals Co., Columbia,
South Carolina; it contained small amounts of impurities
of which a C_6H_6 compound was the most abundant. This
material was purified by a gas chromatographic technique.
A glass column 0.5 m long, 3/8 inch in diameter, and packed
with (Analabs) 60-200 mesh silica gel was connected between
the storage vessel of c-$C_4H_4F_4$ and a chemical high vacuum
line. After the column was evacuated overnight, the vessel
was cooled in a dry ice-isopropanol bath and pumped on for
an hour. The sample was then allowed to warm up to room
temperature. With the arrival of the first traces of gas
the pressure in the vacuum line increased. The first portion
of the gas entering the vacuum line was discarded. The middle
fraction of the purified c-$C_4H_4F_4$, which did not contain any
impurities that could be detected by gas chromatography, was
collected for subsequent use.

Matheson Company C.P. grade ethylene was passed through
a drying tube of barium oxide into a storage vessel on the
vacuum line. Air was removed by repeated freeze-pump-thaw
cycles. Matheson Company research grade oxygen was bled
into the vacuum system through a 1/4 inch drying column of
60-200 mesh reagent grade silica gel.

Sample Irradiation and Dosimetry

The irradiations of the samples were carried out using

a Cobalt-60 gamma irradiator which has been described pre-
viously.[53]   The dose rate in 400 Torr ethylene was determined
by measuring hydrogen production, assuming $G(H_2) = 1.2$.[54]
Gases non-condensible at $-196°C$ were collected via a Toepler
pump, measured on a McLeod gauge, and analyzed for methane
and ethylene content on a flame ionization gas chromatograph
using a silica gel column at room temperature.   Hydrogen
analysis was by difference.   Energy absorbed in $c-C_4H_4F_4$ was
assumed proportional to S, the electron stopping power per
mole,[55,56] relative to ethylene, and $S(c-C_4H_4F_4)/S(c-C_2H_4)$ was
calculated to be 3.81.   The dose rates were 2.14×10^{19} eV
$mole^{-1} hr^{-1}$ in the metal vessel using a 230 Curie source and
5.59×10^{19} eV $mole^{-1} hr^{-1}$ using a 600 Curie source.   The
dose rate in the glass vessel was 6.68×10^{21} eV $mole^{-1} hr^{-1}$;
only the 600 Curie source was utilized.

Sample Preparation for Hydrogen and Organic Yield Measurements

The radiolysis vessels were made of pure nickel cylinders
which were helium arc welded to Monel valves.[29]   For un-
scavenged radiolyses, $c-C_4H_4F_4$ was directly metered into the
nickel vessel which had been pumped down and flamed under
vacuum to decompose any solid products formed in the previous
radiolysis.   Then the vessel was immersed in a Dewar contain-
ing liquid nitrogen and pumped on for five minutes to remove
any air which might have leaked into the vessel during sample
preparation.   This procedure was essential to get reproducible
yields for the olefins, since their yields are very sensitive
to the presence of any scavenger.   In the case of oxygen

scavenged radiolyses the sample was introduced as above, and O_2 was transferred into the liquid nitrogen cooled radiolysis vessel from a standard volume container filled with O_2 at known pressure. By knowing the volume of the vacuum line, the standard container, and the radiolysis vessel, the pressure of O_2 in the radiolysis vessel at room temperature was calculated. In several blank experiments, the amount of O_2 metered out as described was checked using a Toepler pump - McLeod gauge apparatus; the error was found to be less than 5%. In all the irradiations the pressure of $c-C_4H_4F_4$ was 50 Torr, and the pressure of the added O_2 was 4% of the total pressure in the vessel. Also, a few semi-quantitative experiments were carried out with I_2, C_2H_4, or $1,1-C_2H_2F_2$ added to the system as scavengers.

Sample Preparation for HF Yield Measurements

For HF analyses a glass vessel equipped with a break seal was cleaned and annealed at 565° C to pyrolyze any remaining organic residues. In the cases of unscavenged radiolyses required amounts of $c-C_4H_4F_4$ were metered by pressure measurements into a standard vessel of known volume and later transferred into the radiolysis vessel cooled in liquid N_2. The radiolysis vessel was sealed under vacuum.

In cases of O_2 scavenged radiolyses, the $c-C_4H_4F_4$ was introduced as above, a premeasured amount of O_2 from another standard vessel was introduced into the vacuum line, and the vessel was sealed off. The amount of O_2 introduced into the vessel was measured in one blank run utilizing the procedure

described earlier in connection with the metal vessel.

Product Identification

The formation of hydrogen fluoride in the radiolysis
of $c-C_4H_4F_4$ was established by potentiometric titration of
the irradiated sample using a fluoride ion selective elec-
trode. Hydrogen was identified by its retention time on a
13-X molecular sieve column in a gas chromatograph equipped
with a thermal conductivity detector. The organic products
were identified by their mass spectral cracking pattern
using a gas chromatograph - mass spectrometer combination.[42]
When possible the identifications were confirmed by comparison
of retention times with known standards and by matching the
mass spectra with spectra given in the API Tables.[57] The ^{19}F
NMR spectrum of peak 21 recorded using a Varian XL-100 spec-
trometer equipped with NTC Fourier transform accessories.
The spectrum was scanned 2000 times. In most of these iden-
tification procedures, products formed by a spark-discharge
in $c-C_4H_4F_4$ were used, since the yields of the products are
larger than in the radiolysis and the tailing by the parent
peak could be minimized. (In several previous researches
in this laboratory it has been found that products formed in
a very weak Tesla Coil discharge of organic gases are quali-
tatively and even semi-quantitatively similar to those formed
during gamma radiolysis.)[10,53] Standards were available for
most of the lighter products analyzed on the silica gel column,
but not for $C_3H_4F_2$ or $C_3H_2F_4$; there were no available stan-
dards for several of the products measured on the SE-30 column.

In such cases, product identification is somewhat tentative.

Product Analyses

1) Hydrogen fluoride. Hydrogen fluoride was determined by potentiometric titration using a fluoride ion selective electrode. The details of the experiment are given in connection with the photolysis of tetrafluorocyclobutane (Chapter III). Addition of chloride ions to the analyte, necessary for the photolysis work due to the presence of mercury, was not required for the radiolysis samples.

2) Hydrogen. In the unscavenged system, hydrogen was measured as in the case of the dosimetry experiments. However, in the oxygen scavenged experiments, all gases non-condensible at -196° C were Toeplered into a McLeod gauge, and this mixture was analyzed for both the methane and hydrogen content using a gas chromatograph equipped with a flame ionization detector (FID) in tandem with a thermal conductivity detector (TCD). The FID was used for measuring the amount of methane and the TCD for that of hydrogen. The column used was a 13-X molecular sieve column mentioned above, and the carrier gas was nitrogen.

3) Low Molecular Weight Products. The low molecular weight organic products (all compounds with one or two carbon atoms and one compound with three carbon atoms) were analyzed on a 4.6 m stainless steel column packed with 60-80 mesh (Analab) silica gel using a Tracor 550 research gas chromatograph equipped with a flame ionization detector.

4) High Molecular Weight Products. The high molecular

weight organic products (molecules with three or more carbon atoms) were analyzed on a 12 m glass column packed with Chromasorb-W coated with 30% SE-30. The same Tracor gas chromatograph was used. In the chromatographic analysis of both low and high molecular weight organic products, helium was used as the carrier gas. The molar response of all C_1 and C_2 compounds in a flame ionization detector were obtained by using standards which were available. However, the molar response factors of the compounds were estimated from the response of similar compounds.

Results

In all, 24 products were identified and their G values measured in the radiolysis of $c-C_4H_4F_4$. The inorganic species, hydrogen fluoride and hydrogen, were the most abundant products. The yields of both hydrogen fluoride and hydrogen were linear with dose, within experimental error (Figures (16) and (17), respectively). A typical gas chromatogram of the products eluting on the silica gel column is shown in Figure (18). The three major olefins, 1,1-difluoroethylene (1,1-$C_2H_2F_2$), tetrafluoroethylene and ethylene are shown in Figures (19) and (20). C_2H_4 was produced in negligible quantities. The yield of C_2H_4 showed a small induction period and later increased linearly with dose. The yield of 1,1-$C_2H_2F_2$ was small and the dose-yield plot did not extrapolate to zero yield at zero dose. However, an unirradiated sample did not show even a trace of 1,1-$C_2H_2F_2$. The yield-dose plot of
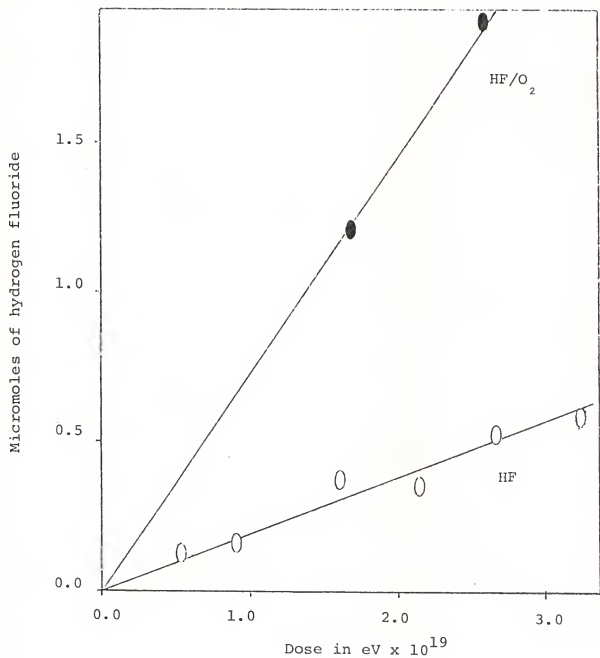
Figure 16. Production of hydrogen fluoride (pure, ○ ; 4% O_2, ●) as a function of dose in the radiolysis of $c\text{-}C_4H_4F_4$.
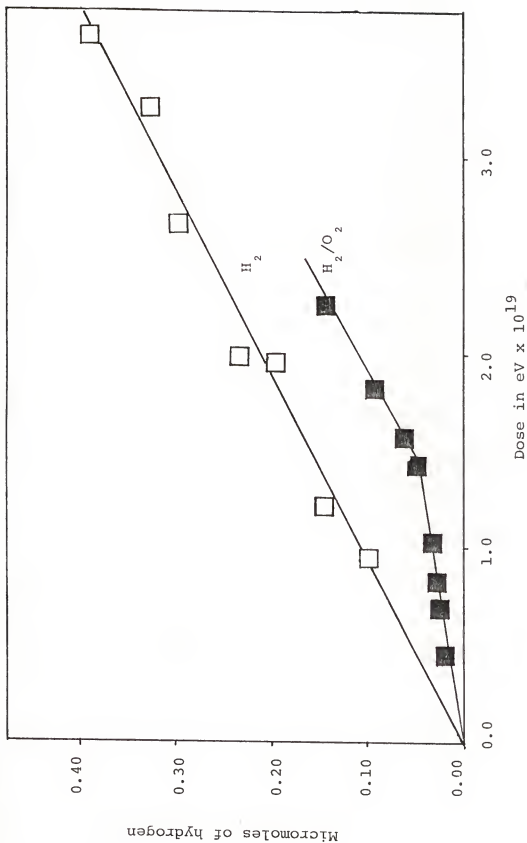
Figure 17. Production of hydrogen (pure, ☐ ; 4% O_2, ■) as a function of dose in the radiolysis of c-$C_4H_4F_4$.
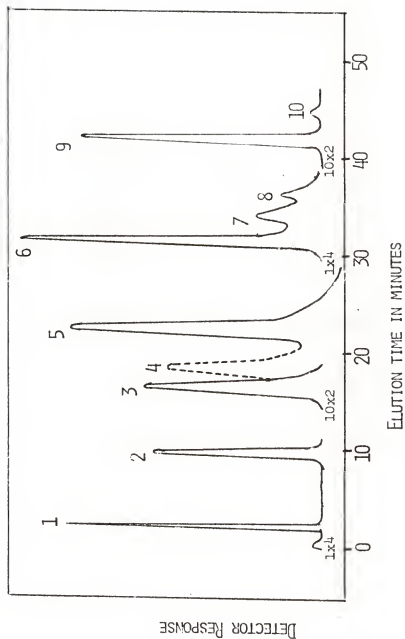
Figure 18. Gas chromatogram of irradiated 1,1,2,2-tetrafluorocyclobutane: low molecular weight products eluting on a Silica Gel column.

1. CH_4
2. C_2H_6
3. C_2F_4
4. C_2H_4

5. $1,1-C_2H_2F_2$
6. C_2H_2
7. C_2H_3F
8. $1,2-C_2H_2F_2$ (trans)

9. $c-C_3H_4F_2$
10. $1,2-C_2H_2F_2$ (cis)

Figure 19. Production of $1,1-C_2H_2F_2$ (pure $\bigcirc$; 4% O_2, $\bullet$) and C_2H_4 (4% O_2, $\blacktriangle$) as a function of dose in the radiolysis of $c-C_4H_4F_4$.
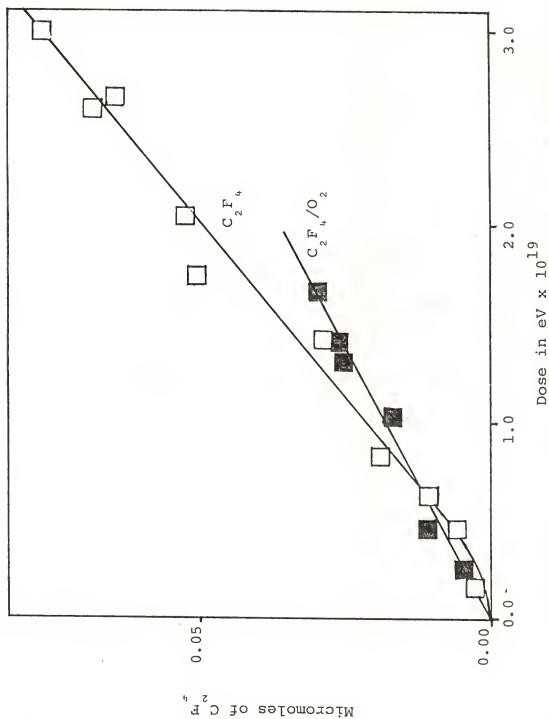
Figure 20. Production of C_2F_4 (pure ☐; 4% O_2, ◼) as a function of dose in the radiolysis of $c\text{-}C_4H_4F_4$.

acetylene (Figure (21)) showed a distinctive break in slope, the yield increasing at a higher rate at longer doses. The G values of all the products eluting on the silica gel column are shown in Table VIII.

A chromatogram of the products eluting on the SE-30 column is shown in Figure (22). The first three peaks were made up of all the products analyzed on the silica gel column except $C_3H_4F_2$. Products 9 and 11 through 14 were identified to be $C_3H_4F_2$, $C_3H_2F_4$, $C_4H_2F_4$, $C_4H_2F_2$ and $C_4H_3F_3$, respectively, based on their mass spectral cracking patterns, obtained using the GC/MS combination as mentioned earlier. The details of the identification are given in Appendix I. Peak 15 was small and neither the composition nor structure of this product could be determined. Peak 16 is probably c-$C_4H_2F_4$. Peaks 18 and 19 were very small and in most of the runs smeared out by the tail of the parent peak. The ^{19}F NMR of Peak 21 is shown in Figure (23). The proton NMR showed the presence of the olefinic hydrogen. Based on the NMR and the mass spectral data Peak 21 was assigned to be:

$$
\begin{array}{cccc}
\text{H} & \text{H} & \text{F} & \text{F} \\
| & | & | & | \\
\text{H}-\text{C}-&\text{C}-&\text{C} = &\text{C} \\
\text{F}-\text{C}-&\text{C}-\text{F} & & \text{H} \\
| & | & & \\
\text{F} & \text{F} & &
\end{array}
$$
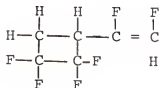
Peak 22 is non-cyclic as shown by its proton NMR. A discussion of the structural determination of many of the other compounds is given in Appendix I.

The G values of all the products measured on the SE-30
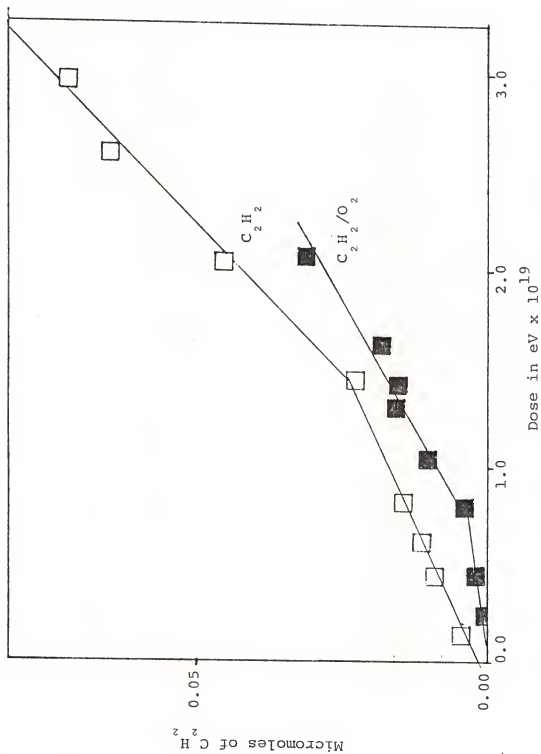
Figure 21. Production of C_2H_2 (pure $\square$; 4% O_2, ▪) as a function of dose in the radiolysis of c-$C_4H_4F_4$.

TABLE VIII

G Values in the Radiolysis of 1,1,2,2-Tetrafluorocyclobutane:
Products Eluting on the Silica Gel Column

Product	Pure System		O_2 Scavenged System	
	Low Dose[a]	High Dose	Low Dose	High Dose
H_2	0.52	0.52	0.205	0.682
HF	2.3	2.3	8.6	8.6
CH_4	0.0082	0.0082	0.008	0.0
C_2H_6	0.0057	0.0129	0.0057	0.0057
C_2F_4	0.093	0.171	0.109	0.109
C_2H_4	0.0	0.0	0.053	0.125
$1,1-C_2H_2F_2$	(~.47)	0.0464	0.471	0.471
C_2H_2	0.0853	0.196	0.0186	0.114
C_2H_3F	0.0125	0.0	0.024	0.0397
$1,2-C_2H_2F_2$	0.0071	0.0071	0.0	0.0
$C_3H_4F_2$	0.023	0.0487	0.0	0.0
$1,2-C_2H_2F_2$	0.0546	0.0546	≤ 0.001	≤ 0.001
C_2HF_3	0.01[c]	0.01[c]	__[b]	—
$C_3H_2F_4$	0.0035	0.0165	≤ 0.001	≤ 0.001
CHF_3	0.01	0.01[d]	—	—

[a] Yields measured at doses below 1 x 10^{19} eV (2 x 10^{19} eV in the case of C_2H_6).

[b] Dash indicates product not measured.

[c] C_2HF_3 eluted with C_2H_2; yield estimated from mass spectrometric analysis.

[d] CHF_3 eluted with $1,1-C_2H_2F_2$; yield estimated from mass spectrometric analysis.
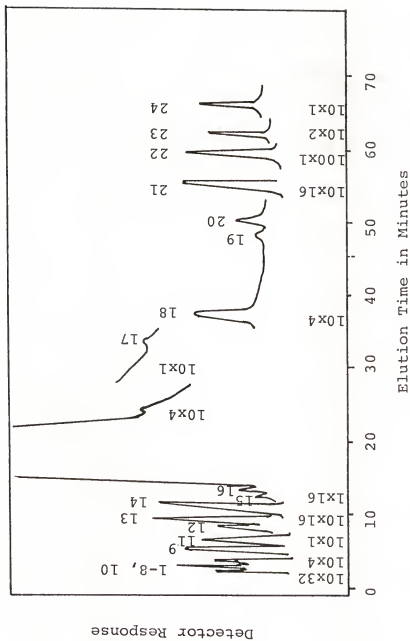
Figure 22. Gas chromatogram of irradiated 1,1,2,2-tetrafluorocyclobutane: high molecular weight products eluting on a SE-30 column.
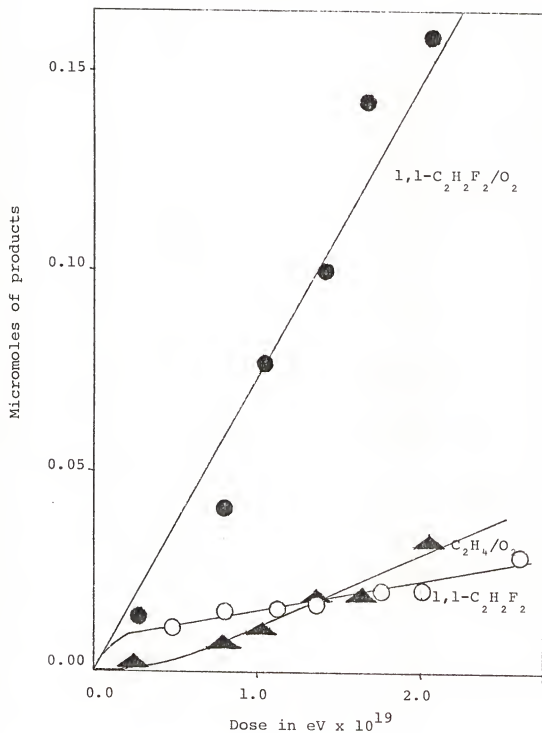
15.-20. C_4–C_6 compounds   24. $C_8H_6F_8$

11. $C_3H_2F_4$
12. $C_4H_2F_4$
13. $C_4F_2F_2$
14. $C_4H_3F_3$

21. $C_6H_4F_6$
22. $C_6H_4F_6$
23. C_8 compound
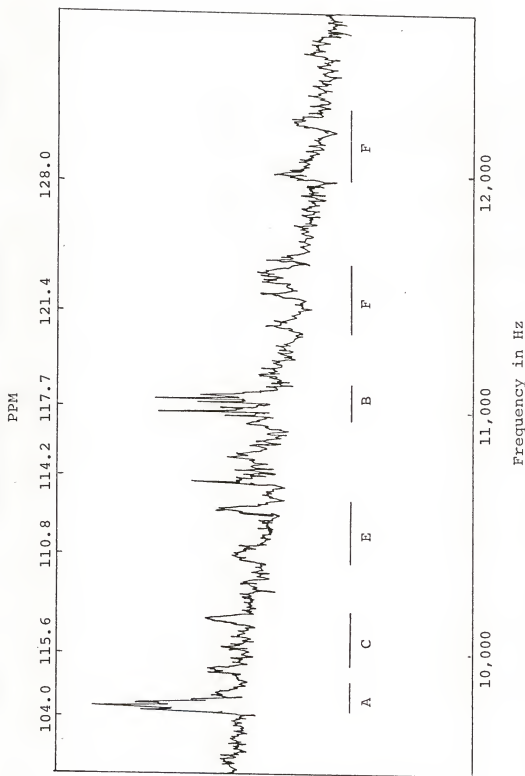
Figure 23. ^{19}F NMR spectrum of product Number 21, $C_6H_4F_6$. The assignments of the peaks are as follows:
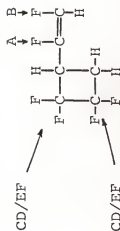
column are shown in Table IX. The yield-dose curves for
$C_4H_3F_3$ (Peak 14) and $C_6H_4F_6$ (Peak 21) are shown in Figure
(24). The yields of both $C_4H_3F_3$ and $C_6H_4F_6$ showed an
induction period and at higher doses increased linearly
with dose.

Addition of oxygen to the system substantially altered
the G values of all but two of the major products, $C_4H_3F_3$
and C_2F_4. The G value of C_2H_4 increased considerably (from
zero to 0.125). The yield showed an induction period and
increased linearly with dose above 0.5×10^{19} eV. The most
dramatic change was in the yield of $1,1-C_2H_2F_2$, which increased
ten-fold from 0.046 to 0.471. The yield of this olefin in-
creased linearly with dose. The acetylene yield was de-
creased upon addition of oxygen. The yield of methane, a
minor product, showed an interesting plateau above 1×10^{19} eV
in the presence of oxygen.

The G values of products eluting on the SE-30 column
in the oxygen scavenged system were small; moreover, they
elute between unidentified oxygenated compounds. Hence,
we could only estimate an upper limit for these yields.

The G values of HF in C_2H_4 and I_2 scavenged systems
were 1.6 and 1.8, respectively. The G values of all measured
products in the I_2 scavenged system are given in Table X.

Material Balance

Material balance is not very satisfactory in this system.
The ratio of C/H/F is 4.0/6.2/6.3. It is evident that there
is a shortage of carbon. We attribute this shortage mostly
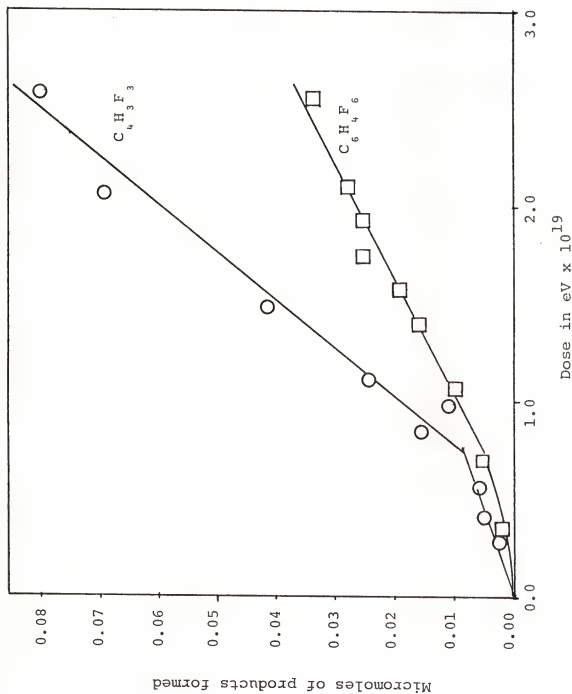
Figure 24. Production of $C_4H_3F_3$ (pure O) and $C_6H_4F_6$ (pure □) as a function of dose in the radiolysis of $c-C_4H_4F_4$.

TABLE IX

G Values in the Radiolysis of 1,1,2,2-Tetrafluorocyclobutane:
Products Eluting on the SE-30 Column

| Product | Pure System | | O_2 Scavenged System |
	Low Dose	High Dose	
$C_3H_4F_2$[a]	0.032	0.047	0.005
$C_3H_2F_4$	0.013	0.021	0.005
$C_4H_2F_4$	0.0062	0.017	<<0.001
$C_4H_2F_2$	0.013	0.013	<<0.001
$C_4H_3F_3$	0.063	0.197	0.13[b]
$C_5H_6F_4$	0.007	0.05	___[c]
?	0.01	0.01	___
?	___	0.05	___
$C_6H_4F_6$	0.05	0.09	~0.05[d]
$C_6H_4F_6$	0.02	0.06	~0.05[d]
?	0.0	0.015	<<0.001
$C_8H_6F_8$	0.01	0.0	0.0

[a]Measured on silica gel column also.

[b]Based on the first three points. (The yield at longer doses
becomes zero and then becomes negative.)

[c]Dash indicates product not measured.

[d]Irreproducible.

TABLE X

G Values of Products in I_2 Scavenged Radiolysis
of 1,1,2,2-Tetrafluorocyclobutane

Product	G Value
HF[a]	1.8
H_2	0.28
C_2H_6	<0.005
C_2F_4	0.10
C_2H_4	0.01
$1,1-C_2H_2F_2$	0.60
C_2H_2	0.14
C_2H_3F	0.09
$C_4H_3F_3$	0.12

[a]The G value of HF in C_2H_4 scavenged system is 1.6.

to the formation of polymers which were not analyzable by the methods employed in this research. The formation of polymers was indicated by the evolution of a large amount of fluorine-containing organic fragments when a vessel which had been irradiated with the compound inside it was attached directly to the mass spectrometer and flamed strongly with a hand torch. We expect some contribution to this carbon deficit from un-analyzed products which may have eluted with the parent compound.

Discussion

From the results of our studies of ion-molecule reactions in $c\text{-}C_4H_4F_4$ it is evident that the most abundant positive ion at higher pressures is $C_2H_2F_2^+$. If we assume a typical W value of 33 eV/ion pair for this system,[59] the value of $G(C_2H_2F_2)$ should be approximately 2.5 because the abundance of $C_2H_2F_2^+$ at higher pressures is of the order of 85% of the total ion intensity. A W value of 33 would imply a G value of 3 for the decomposition of $c\text{-}C_4H_4F_4$ through ionic primary processes. The value $G(-M) = 3$ is in accordance with that expected for a partially fluorinated hydro-carbon where C-C and C-H bond ruptures predominate and the net decomposition is moderate.[60] Stoichiometric considerations lead to a G value of 2.5 for $C_2H_2F_2$ in the primary step.

$$c\text{-}C_4H_4F_4 \rightsquigarrow C_2H_2F_2^+ + C_2H_2F_2 + e^- \qquad \text{IV.(1)}$$
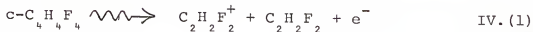
Whereas $C_2H_2F_2^+$ is observed to be the predominate positive

ion in the system, theoretical arguments indicate that F^- must be the most abundant negative entity. The electron affinity of fluorine atom is so large (3.6 eV) that dissociative electron attachment leading to the formation of F^- would be a very low energy process.[61]

$$c\text{-}C_4H_4F_4 + e^- \longrightarrow C_4H_4F_3\cdot + F^- \qquad\qquad \text{IV.(2)}$$

A reasonable value for the C-F bond strength in a cyclobutane would be about 110 kcal/mole. Using this value of bond strength and the electron affinity of $F\cdot$ we calculate the threshold of Reaction IV.(2) to be not greater than 2 eV. Hence, the neutralization of these two ions, $C_2H_2F_2^+$ and F^-, is expected to play a major role in the radiolysis.

$$C_2H_2F_2^+ + F^- \longrightarrow (C_2H_2F_3)^* \longrightarrow C_2HF_2\cdot + HF$$
$$\text{IV.(3)}$$
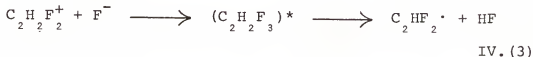
This reaction could also proceed directly via H^+ transfer to F^- (i.e., a stripping process):

$$C_2H_2F_2^+ + F^- \longrightarrow C_2HF_2\cdot + HF \qquad\qquad \text{IV.(4)}$$
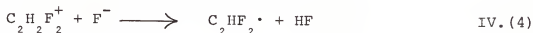
The HF formed in Reactions IV.(3) and IV.(4) would be unscavengeable by radical scavengers since it is formed in an ionic acid-base reaction. If we attribute most of the unscavengeable HF to this reaction, the G value of F^- would be approximately 1.5, which appears reasonable.

The $C_2H_2F_2$ not neutralized by F^- should be neutralized by the only other plausible negative species in the system, the electron.

$$C_2H_2F_2^+ + e^- \longrightarrow (C_2H_2F_2)^* \qquad \text{IV.(5)}$$
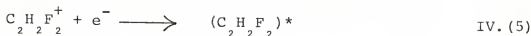
The magnitude of $G(C_2H_2F_2)^*$ would be about 1.0 since the rest of the $C_2H_2F_2^+$ (G=1.5) would have been neutralized by F^-. The excited $C_2H_2F_2$ formed in Reaction IV.(5) should have an excess energy of 10.12 eV (the ionization potential of $C_2H_2F_2$). This amount of energy is sufficient to break any of the bonds in $C_2H_2F_2$. However, the C=C double bond is considerably stronger than either C-F or C-H (145 kcal versus 108 and 98 kcal, respectively) and its rupture appears unlikely in spite of the considerable energy excess.

$$(C_2H_2F_2)^* \longrightarrow C_2HF \cdot + H \cdot \qquad \text{IV.(6)}$$

$$(C_2H_2F_2)^* \longrightarrow C_2H_2F \cdot + F \cdot \qquad \text{IV.(7)}$$
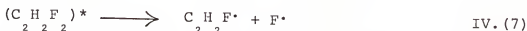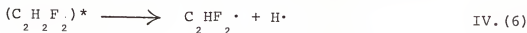
In difluoroethylene the C-F bond strength should be about 110 kcal/mole and the C-H bond strength about 95 kcal/mole. The internal energy of $(C_2H_2F_2)^*$ would be so large compared to the difference in the bond strength of C-F and C-H bonds that there might be very little specificity in breaking of one bond over the other. However, we expect Reaction IV.(6) to be somewhat more probable than Reaction IV.(7) since $C_2HF_2 \cdot$ would be more stable than $C_2H_2F \cdot$. Another possible mode of decomposition of $(C_2H_2F_2)^*$ would be HF elimination.

$$(C_2H_2F_2)^* \longrightarrow H-C\equiv C-F + HF \qquad \text{IV.(8)}$$

It is interesting to note that we did see a product whose mass spectrum was similar to that of C_2HF,[62] but the yields

of this compound were very small and irreproducible, probably due to its lability.

Since the postulated G value of $(C_2H_2F_2)*$ is 1.0, the G values for production of $F\cdot$ and $C_2HF_2\cdot$ in Reaction IV.(7) would be less than 0.5 and those for $H\cdot$ and $C_2HF_2\cdot$ in Reaction IV.(6) would be greater than 0.5. Hence, the total G value for $C_2HF_2\cdot$ in Reactions IV.(3) and IV.(4) should be greater than 2.0. We will come back to the discussion of the fate of these radicals later in this section.

Equation IV.(1) shows the "symmetrical" rupture of parent $c\text{-}C_4H_4F_4$ into two difluoroethylenic species. The other two olefins, C_2F_4 and C_2H_4 are also certainly formed by the direct decomposition of $c\text{-}C_4H_4F_4$ (in either an ionic or excited state). The increase in the G value of $1,1\text{-}C_2H_2F_2$ (from 0.046 to 0.47) and C_2H_4 (from 0.0 to 0.125) upon addition of oxygen to the systems indicates that these two olefins are labile under radiolytic conditions. However, even the measured yields in the O_2 scavenged system do not reflect the primary yields of these species, especially that of $C_2H_2F_2$. The relatively small yields of ethylenic products indicate that there may be polymerization of these compounds under free radical attack leading to products not detected in our experiments. As discussed in the section on material balance, we did see a large amount of fluorinated compounds coming off the vessel walls when heated, indicating the formation of polymers. Oxygen is known to react with fluorinated radicals to form peroxy radicals which usually decompose

to give other radicals.[63] These other radicals can initiate
the polymerization even in the presence of oxygen. Hence,
the small yield of olefins in the presence of O_2 is not
very revealing.

In the pure system, however, we expect $C_2HF_2 \cdot$ (the most
abundant radical in the system) to initiate polymerization
of the olefins.

$$C_2H_2F_2 + C_2HF_2 \cdot \longrightarrow C_4H_3F_4 \cdot \qquad \text{IV.(9)}$$

$$C_2H_2F_2 + C_4H_3F_4 \cdot \longrightarrow C_6H_5F_6 \cdot \qquad \text{IV.(10)}$$
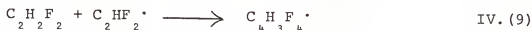
Chain termination reactions would include

$$2\ C_2HF_2 \cdot \longrightarrow C_4H_2F_4 \qquad \text{IV.(11)}$$

$$C_2HF_2 \cdot + C_4H_3F_4 \cdot \longrightarrow C_6H_4F_6 \qquad \text{IV.(12)}$$

$$2\ C_4H_3F_4 \cdot \longrightarrow C_8H_6F_8 \qquad \text{IV.(13)}$$
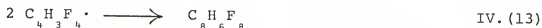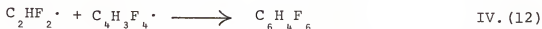
—etc.—

The yield-dose plots of $C_8H_6F_8$ and product 23 level off at
higher doses indicative of further reactions. This type
of polymerization has been seen in many olefinic systems,
such as C_2F_4[64] and C_2H_4.[65] A similar polymerization scheme
has been postulated in the radiolysis of c-C_4F_8.[10] In
addition, it is very likely that there could be ionic poly-
merization of $C_2H_2F_2^+$ similar to that seen in the ethylene
system.[66] Although the limited data available do not justify
further speculation concerning polymerization processes, the

proposed reaction scheme does provide a reasonable explanation
of the formation of several products including $C_4H_2F_4$, $C_6H_4F_6$,
$C_8H_6F_8$, etc.

In the presence of oxygen, the yields of $1,1-C_2H_2F_2$ and
C_2H_4 are markedly increased relative to the pure system. In
the unscavenged system the yield of C_2F_4 shows an initial
linear region with G = 0.093, shifting to a second essentially
linear region with the considerably larger yield of G = 0.171
at high dose. With added oxygen, the tetrafluoroethylene
yield is linear throughout, with G = 0.109. Since a direct
route to C_2F_4 production would be independent of dose range,
it is apparent that there must be a second route to tetra-
fluoroethylene production which is blocked by the presence
of scavengers. It should be noted that the yield of $C_2H_2F_2$
is much greater than those of either C_2F_4 or C_2H_4; the
difference is considerably beyond the statistical expectation
of 2:1:1. An interpretation of the relatively large yield
of $C_2F_2H_2$, based upon unimolecular fragmentation theory, is
given in Appendix II.

The decrease in the yield of H_2 in the I_2 scavenged
system (G(H_2)=0.28) and at lower doses in the oxygen scavenged
system shows that a part of the hydrogen yield is scavengeable.
The remainder must come from molecular elimination reactions,
ionic processes, or hot hydrogen atom abstraction from the
substrate. $C_4H_4F_4$* formed either by direct excitation or
neutralization of $C_4H_4F_4^+$ could undergo a C-H bond scission to
give either hot or thermal atoms.

$$c\text{-}C_4H_4F_4 \rightsquigarrow (C_4H_4F_4)^* \qquad \text{IV.(14)}$$

$$C_4H_4F_4^+ + e^- \longrightarrow (C_4H_4F_4)^* \qquad \text{IV.(15)}$$

$$(C_4H_4F_4)^* \longrightarrow C_4H_3F_4 \cdot + H\cdot \qquad \text{IV.(16)}$$
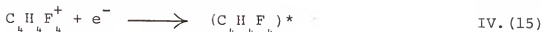
The sequence (Reactions IV.(14) and IV.(16)) may be moderately important but Reactions IV.(15) and IV.(16) probably contribute very little to the hydrogen yield, in comparison to Reaction IV.(6), since $C_4H_4F_4^+$ ion has a low abundance in the mass spectrum of $c\text{-}C_4H_4F_4$.

The molecular processes leading to the formation of H_2 would include

$$(C_4H_4F_4)^* \longrightarrow C_4H_2F_4 + H_2 \qquad \text{IV.(17)}$$

and

$$(C_2H_4)^* \longrightarrow C_2H_2 + H_2 \qquad \text{IV.(18)}$$
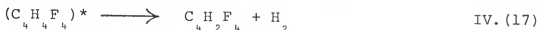
Molecular hydrogen elimination by excited ethylene is well known. In Chapter I, we have postulated that $c\text{-}C_4H_4F_4^+$ undergoes fission through a concerted reaction to give $C_2F_4^+$ and C_2H_4 or $C_2H_4^+$ and C_2F_4. The excess energy content of the reaction intermediate would be probably greater than the endoergicity of the reaction and would leave behind an excited C_2H_4 or $C_2H_4^+$. Hence, Reaction IV.(18) (or its ionic analog) could certainly follow. Since we contend that most of the acetylene yield is formed through hydrogen elimination by ethylene, the sum of the yields of C_2H_2 and $C_2H_2F_4$ should approximately equal the yield of H_2 in the scavenged system;

in fact, this is found to be true. We do not have a definite explanation for the increase in hydrogen yield at larger doses in the presence of oxygen; this may be due to the reactions of oxygenated radicals.

Hydrogen fluoride is the most abundant product in the radiolysis of $c\text{-}C_4H_4F_4$ with $G(HF) = 2.3$. About 25% of this yield is scavengeable by either C_2H_4 or I_2; this HF must come from the reaction of $H\cdot$ atoms formed in reactions such as in Equation IV.(6).

$$H\cdot + c\text{-}C_4H_4F_4 \longrightarrow HF + C_4H_4F_3\cdot \qquad \text{IV.(19)}$$
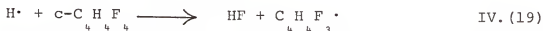
The increase in HF yield in the presence of oxygen is most likely due to oxygenated radicals. It is known that O_2 reacts with $F\cdot$, $H\cdot$, etc. forming very reactive radicals,[42] which can attack the substrate leading to the formation of CO, FCOF, etc., many of which will end up on the wall as fluorides.[67] The unscavengeable HF is probably formed mainly through molec-ular HF elimination, ionic reactions, and abstraction by F atoms. Fluorine atoms are certainly formed in this system and could react with the substrate through either $H\cdot$ atom ab-straction or ring opening. The HF formed by $H\cdot$ atom ab-straction would be unscavengeable by any additive at moderate concentrations, since the reaction is exoergic by approximately 25 kcal; there is no reason to expect an unfavorable steric factor. The four-centered hydrogen halide elimination is well known.[68] This HF elimination, presumably by $C_4H_4F_4$*, would give either a cyclic $C_4H_3F_3$ or a straight chain isomer of $C_4H_3F_3$.

$$(C_4H_4F_4)^* \longrightarrow C_4H_3F_3 + HF \qquad \text{IV.(20)}$$

The product identified to be $C_4H_3F_3$ (product 14) is formed
mostly by HF molecular elimination as suggested by the fact
that its G value is not substantially altered in the presence
of O_2, C_2H_4, I_2 or $1,1-C_2H_2F_2$ additives. However, we contend
that most of the unscavengeable HF comes not from molecular
eliminations but from ion neutralization (Reactions IV.(3)
and IV.(4)). This ionic yield would also be unscavengable by
C_2H_4 and I_2.

There are two C_3 compounds and the sum of their yields
[G(sum)=0.068] is very much greater than the sum of the yields
of C_1 compounds. However, if product 18 is formed through
Reaction IV.(25) only, then the sum of the yields of $C_5H_6F_4$,
CH_4, and CHF_3 would be 0.068 which shows mass balance for
these products. In this argument it is assumed that $C_4H_4F_4$
undergoes a scission to give a C_1 and a C_3 species.

$$(C_4H_4F_4)^* \longrightarrow C_3HF_4\cdot + CH_3\cdot \qquad \text{IV.(21)}$$

$$(C_4H_4F_4)^* \longrightarrow C_3H_4F\cdot + CF_3\cdot \qquad \text{IV.(22)}$$

$$CH_3\cdot + c\text{-}C_4H_4F_4 \longrightarrow CH_4 + C_4H_3F_4\cdot \qquad \text{IV.(23)}$$

$$CF_3\cdot + c\text{-}C_4H_4F_4 \longrightarrow CHF_3 + C_4H_3F_4\cdot \qquad \text{IV.(24)}$$

$$CH_3\cdot + C_4H_3F_4\cdot \longrightarrow C_5H_6F_4 \qquad \text{IV.(25)}$$

$$C_3HF_4\cdot + c\text{-}C_4H_4F_4 \longrightarrow C_3H_2F_4 + C_4H_3F_4\cdot \qquad \text{IV.(26)}$$

$$C_3H_4F\cdot + c\text{-}C_4H_4F_4 \longrightarrow C_3H_4F_2 + C_4H_4F_3\cdot \qquad \text{IV.(27)}$$
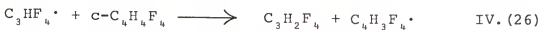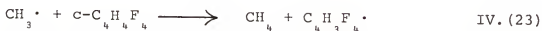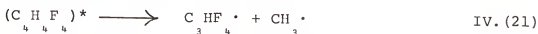
It is very likely that other abstraction, combination and disproportionation reactions occur.

Formation of C_2H_6 quite likely proceeds through hydrogen atom reaction with C_2H_4.

$$C_2H_4 + H\cdot \longrightarrow C_2H_5\cdot \qquad \text{IV.(28)}$$

$$C_2H_5\cdot + c\text{-}C_4H_4F_4 \longrightarrow C_2H_6 + C_4H_3F_4\cdot \qquad \text{IV.(29)}$$

The source of these hydrogen atoms would be Reactions IV.(6) and IV.(16). We cannot rule out a two step ring opening/ fragmentation under hydrogen atom attack to form $C_2H_5\cdot$ as in the case of mercury sensitized photolysis. The amount of C_2H_6 formed is too large compared to CH_4 to consider two methyl radicals combining to give C_2H_6 as a significant process.

The formation of other minor products, C_2H_3F, C_2F_3H, 1,2-$C_2H_2F_2$, $C_4H_2F_2$, etc., can be explained either by the reaction of $C_2HF_2\cdot$ or $C_2H_2F\cdot$ abstracting either a $F\cdot$ or $H\cdot$ from the substrate or by radical combinations.

$$C_2HF_2\cdot + c\text{-}C_4H_4F_4 \longrightarrow C_2HF_3 + C_4H_4F_3\cdot \qquad \text{IV.(30)}$$

$$C_2HF_2\cdot + c\text{-}C_4H_4F_4 \longrightarrow 1,2\text{-}C_2H_2F_2 + C_4H_3F_4\cdot \qquad \text{IV.(31)}$$

$$C_2H_2F\cdot + c\text{-}C_4H_4F_4 \longrightarrow C_2H_3F + C_4H_3F_4\cdot \qquad \text{IV.(32)}$$

$$C_2H_2F\cdot + C_2HF_2\cdot \longrightarrow (C_4H_3F_3)^* \longrightarrow C_4H_2F_2 + HF \qquad \text{IV.(33)}$$
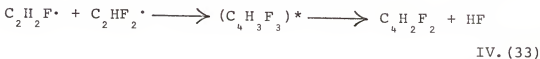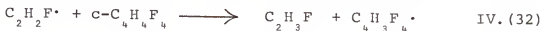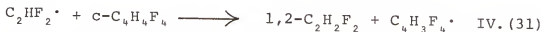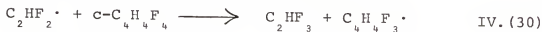
The radical $C_4H_4F_3\cdot$ could also abstract a hydrogen from the

substrate.

$$C_4H_4F_3 \cdot + c\text{-}C_4H_4F_4 \longrightarrow C_4H_5F_3 + C_4H_3F_4 \cdot \qquad \text{IV.(34)}$$

However, we have not seen this $C_4H_5F_3$ compound. It probably elutes with the parent as discussed in the section on mass balance.

A comparison of the radiation chemistry of cyclobutane, 1,1,2,2-tetrafluorocyclobutane, and perfluorocyclobutane is of interest in understanding the effect of fluorine atoms in a cyclobutane ring. (It is to be noted that, unlike the cases of other halogens, the C-F bond is stronger than the C-H bond.) The stability of the cyclobutanes increases with the increase in the number of fluorine atoms in the compound (i.e., $-\Delta H_f(c\text{-}C_4H_8) < -\Delta H_f(c\text{-}C_4H_4F_4) < -\Delta H_f(c\text{-}C_4F_8)$),[51] [69] [52] which is reflected by the appropriate trend in the net radiolytic decomposition of these compounds, since $G(-\ c\text{-}C_4H_8) \simeq 4$, $G(-\ c\text{-}C_4H_4F_4) \simeq 3$, and $G(-\ c\text{-}C_4F_8) < 3$. One of the primary modes of decomposition in all three cyclobutanes is a scission of the ring to give two olefins. This scission is most prominant in $c\text{-}C_4H_8$ and least in $c\text{-}C_4F_8$. (In both the $c\text{-}C_4H_8$ and $c\text{-}C_4F_8$ systems only one olefin can be formed by the concerted rupture of the ring, unlike $c\text{-}C_4H_4F_4$ where three different olefins, C_2H_4, 1,1-$C_2H_2F_2$, and C_2F_4, are produced.)

Another similarity is the ring opening under radical-atom attack which takes place in all three above mentioned cyclobutanes. Both H· and F· atoms can be formed in

tetrafluorocyclobutane, and both the atoms are expected to open up the ring.

There is one very marked difference between c-$C_4H_4F_4$ on the one hand and c-C_4H_8 and c-C_4F_8 on the other, in that HF is the most abundant product in the c-$C_4H_4F_4$ system, while it can not be formed in the other two cases. The c-$C_4H_4F_4$ system resembles other partially fluorinated alkanes in the formation of HF as a major product of radiolysis.[70]

APPENDICES

APPENDIX I

IDENTIFICATION OF PRODUCTS

In this section the deduction of the composition and, where possible, the structure of the products formed in the radiolytic and/or photolytic studies is discussed. The mass spectral cracking patterns of the products formed in a spark-discharge of $c\text{-}C_4H_4F_4$ are the main source of data. A second general approach is based upon the injection of a series of known compounds on a SE-30 GLC column and determination of the resulting elution times. This procedure was helpful in determining the number of carbon atoms in each product, since elution times on a SE-30 column are dependent mainly on the boiling points of the compounds. Thus, it was possible to correlate the elution times with the carbon numbers of the compounds.

In several instances, comparison of the elution times on two or more gas chromatographic columns was helpful in product identification. This procedure was particularly valuable in establishing the olefinic character of several low molecular weight products, which are selectively retarded on a column made of propylene glycol saturated with silver nitrate.[71] Comparison of tentative product identifications with predictions of a plausible reaction mechanism is often

informative, but this approach must be used with caution since it involves cyclical arguments. Ultimately, however, most of the identifications depend on mass spectral cracking patterns. Unfortunately, only a few partially fluorinated compounds are listed in the API mass spectral tables[57] or in Majer's article on the mass spectroscopy of fluorine compounds.[21] Accordingly, several of the product assignments listed below are tentative.

In all, 24 organic products were detected in the gamma-radiolysis of 1,1,2,2-tetrafluorocyclobutane. Since this group includes all of the products formed in the mercury sensitized photolysis, it is possible to discuss product identification comprehensively with reference to the radiolysis experiments alone. In the case of the majority of the products which eluted on the silica gel column, standards were available and product identifications are definite. Included in this group are the following: Peak 1, CH_4; Peak 2, C_2H_6; Peak 3, C_2F_4; Peak 4, C_2H_4; Peak 5, 1,1-$C_2H_2F_2$; Peak 6, C_2H_2; Peak 7, C_2H_3F; and Peaks 8 and 10, 1,2-$C_2H_2F_2$ (trans and cis isomers, respectively).

The section below describes our conclusions concerning the identify of the remaining radiolysis products, all of which can be separated on the SE-30 column. As mentioned above, the identifications are largely based on mass spectral cracking patterns. Good spectra were obtained for Peaks 9-14 and 21-24; these are listed in Table XI. The spectrum listed for Peak 10 is actually that of a known sample of cis 1,2-

difluoroethylene. It was not possible to obtain useful spectra of Peaks 15-20 due to interference by the parent tetrafluorocyclobutane.

Peak No. 9, $C_3H_4F_2$. Peak 78 clearly corresponds to the molecular ion. The loss of a hydrogen atom or a fluorine atom gives Peak 77 or 59. The loss of both fluorine atoms gives Peak 40 and a loss of CF_2 (50) gives the base peak. This compound was retained by silver nitrate column indicating that it is an olefin.

Peak No. 10, cis 1,2-$C_2H_2F_2$. A standard was available for this compound. The mass spectrum and the elution time of this product corresponds to those of the standard.

Peak No. 11, c-$C_3H_2F_4$. The base peak is the parent peak. Elimination of a CF_2 group (50) gives Peak 64 which is quite intense. This compound was not retained by the silver nitrate column and hence is not an olefin; the only plausible identification is c-$C_3H_2F_4$. Furthermore, the moderate abundance of the parent ion indicates the cyclic nature of this compound.

Peak No. 12, $C_4H_2F_4$. The base peak is $C_3H_2F^+$, formed by the elimination of CF_3. The parent ion is at 126 and the loss of 19 (fluorine) gives 107. This type of fluorine loss is very common in fluorocarbon mass spectral cracking patterns. The retention time of this compound on the SE-30 column shows that it is C_4 species. The compound is not 1,1,2,2-tetra-fluorocyclobutene since the retention times of the two do not match.

Peak No. 13, $C_4H_2F_2$. We are not sure of the composition of this product. Its yield was too small to obtain a good spectrum. It eluted between two C_4 compounds on the SE-30 column and hence we assume it to be a C_4 species. The heaviest peak is at mass 88 and therefore we suggest that it has the empirical formula $C_4H_2F_2$.

Peak No. 14, $C_4H_3F_3$. The heaviest peak is at mass 108, the parent peak. The base peak is at mass 50, and is probably CF_2^+ or more likely a combination of CF_2^+ and $C_4H_2^+$. The peak at 57 ($C_3H_2F^+$) is formed by the elimination of CHF_2, probably indicating the presence of such a group in the molecule. The absence of a peak at 64 ($C_2H_2F_2^+$) indicates that this is not 2,3,3-trifluorocyclobutene.

Peaks 15-20. These products eluted either just before, or on the tail of the parent compound. Hence, we could not obtain a useful mass spectrum of any of them. Since Peaks 15 and 16 eluted just before the parent, a C_4 compound, we assume that these two are C_4 species. Peak 20 could be a C_6 species with the others being either C_4 or C_5 compounds.

Peak No. 21, $C_6H_4F_6$. The heaviest ion is the parent ion, $C_6H_4F_6^+$. The base peak is at mass 89 ($C_4H_3F_2^+$) formed by the elimination of F^- during formation of the radical ion $C_4H_3F_3^+$ (elimination of fluorine atom is also possible). The second largest peak is at 127 ($C_4H_3F_4^+$) which is formed by the elimination of C_2HF_2 from $C_6H_4F_6$. The similarity between the cracking pattern of this compound and that of c-$C_4H_4F_4$ indicates the presence of a cyclic ring similar to that in c-$C_4H_4F_4$.

The absence of a peak at 28 (C_2H_4) and the presence of peaks at 100 (C_2F_4) and 64 ($C_2H_2F_2$) indicates that there is no C_2H_4 group in the molecule (like that in c-$C_4H_4F_4$) and that c-$C_4H_3F_4$ is a part of this compound. This information leads us to write the structure of Peak No. 21 as c-$C_4H_3F_4$-C_2HF_2. The ^{19}F NMR spectrum of this compound confirms this structure and indicates that the two fluorine atoms in the side chain are on two different carbon atoms in a position cis to each other. Hence, the structure of this product is:

$$
\begin{array}{c}
\quad \text{F} \quad\quad \text{H} \quad\quad \text{F} \quad\ \text{F} \\
\quad | \quad\quad | \quad\quad\ | \quad\ | \\
\text{F--C----C----C} == \text{C} \\
\quad | \quad\quad | \quad\quad\ \quad\quad | \\
\text{F--C----C--H} \quad\quad \text{H} \\
\quad | \quad\quad | \\
\quad \text{F} \quad\quad \text{H}
\end{array}
$$
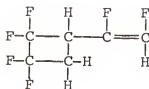
<u>Peak No. 22, $C_{6-4}F_{-6}$</u>. The cracking pattern of this compound and the one in Peak No. 21 are very similar except for the base peak which is one mass heavier. This compound was shown to be linear by its proton NMR spectrum.

<u>Peak No. 24, a C_8 compound</u>. The mass spectral cracking pattern of this compound is not very helpful in assigning a structure for it. The abundance of this product was not sufficient to obtain an NMR spectrum for it. The elution time on the SE-30 column indicated that it is a C_8 compound.

<u>Peak No. 24, $C_8H_6F_8$</u>. The base peak is at mass 89 and the heaviest peak is at 127. This spectrum is very similar to that of c-$C_4H_4F_4$, Peak No. 21 and 22. This indicates the presence of c-$C_4H_3F_4$ group in the structure of this compound.

Its elution time shows that it is a C_8 compound. Hence, we conclude that it is $C_8H_6F_8$, a dimer of $C_4H_3F_4$.

TABLE XIa

Mass Spectral Cracking Patterns of Products

m/e	Assignment	Intensities[a]					
		Peak 9	Peak 10	Peak 11	Peak 12	Peak 13	Peak 14
14	CH_2	58	1	–	–	–	–
25	C_2H	3	14	–	–	–	22
26	C_2H_2	15	17	–	–	–	–
27	C_2H_3	24	–	–	–	–	–
28	C_2H_4	100	–	–	–	–	–
31	CF	14	15	10	32	24	8
32	CHF	–	51	–	–	–	2
33	CH_2F	–	31	–	–	–	–
36	C_3	–	–	–	–	–	12
37	C_3H	–	–	–	–	61	18
39	C_3H_3	–	–	–	–	–	7
40	C_3H_4	46	–	–	–	–	–
43	C_2F	–	6	–	–	–	–
44	C_2HF	–	65	–	–	–	–
45	C_2H_2F	–	100	–	–	–	–

m/e	Formula						
49	C_4H	–	–	–	–	–	48
50	CF_2, C_4H_2	–	–	9	–	–	100
51	CHF_2, C_4H_3	28	–	66	–	–	–
57	C_3H_2F	–	–	–	100	20	16
59	C_3H_4F	22	16	–	–	–	–
64	$C_2H_2F_2$	–	–	89	–	21	–
68	C_4HF	–	–	–	–	54	–
75	C_3HF_2	–	–	–	42	–	–
77	$C_3H_3F_2$	59	–	41	–	–	–
78	$C_3H_4F_2$	40	–	–	–	–	–
87	C_4HF_2	–	–	–	–	–	16
88	$C_4H_2F_2$	–	–	–	–	100	–
107	$C_4H_2F_3$	–	–	–	37	–	–
108	$C_4H_3F_3$	–	–	–	–	–	13
114	$C_3H_2F_4$	–	–	100	–	–	–
126	$C_4H_2F_4$	–	–	–	21	–	–

a Intensities normalized to the largest peak=100.

TABLE XIb

Mass Spectral Cracking Patterns of Products

m/e	Assignment	Intensities[a]			
		Peak 21	Peak 22	Peak 23	Peak 24
14	CH_2	–	–	–	3
27	C_2H_3	7	7	17	1
28	C_2H_4	–	–	13	–
39	C_3H_3	12	13	19	19
51	CHF_2	18	18	58	25
54	C_4H_6	–	9	–	–
57	C_3H_2F	14	–	–	19
59	C_3H_4F	–	–	39	–
64	$C_2H_2F_2$	10	21	88	36
69	CF_3 , C_4H_2F	16	14	–	–
75	C_3HF_2	14	15	–	–
77	$C_3H_3F_2$	4	15	–	–
89	$C_4H_3F_2$	100	–	–	100
90	$C_4H_4F_2$	–	100	–	–
95	$C_3H_2F_3$	20	23	7	24
100	C_2F_4	9	8	29	–
113	C_3HF_4	12	–	100	–
121	C_5HF_4	–	10	–	–
127	$C_4H_3F_4$	53	53	–	43
141	$C_5H_5F_4$	–	–	21	–
177	$C_5H_3F_6$	–	–	21	–
190	$C_6H_4F_6$	10	12	–	–

[a] Intensities normalized to the largest peak=100.

APPENDIX II

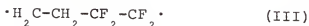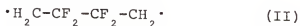UNIMOLECULAR FRAGMENTATION OF CYCLOBUTANE COMPOUNDS

The thermal decomposition of cyclobutanes (cyclobutane itself and substituted cyclobutanes) into two olefinic products has been extensively studied. Benson has shown that these results are in agreement with the formation of a tetramethylene biradical intermediate followed by a C-C bond rupture to give two olefins.[51] This sequential two step scission is aided by the electronic rearrangements in the tetramethylene biradical. Also, this postulate is compatible with Woodward-Hoffman rules as the C_2 symmetry of the cyclobutane ring can be conserved throughout the reaction.

We expect excited $c-C_4H_4F_4$ to follow a similar decomposition scheme even under radiolytic conditions. In radiolysis the secondary processes follow thermal equilibrium kinetics, unlike the primary processes. Assuming that one of the species formed in the primary processes is an excited $c-C_4H_4F_4$ molecule $(c-C_4H_4F_4)^*$ the above mentioned scheme of reaction, and symmetry considerations, can be applied in explaining the amounts of olefinic end products formed in the radiolysis.

We can apply the Woodward-Hoffman rules to the

decomposition of $(c\text{-}C_4H_4F_4)^*$ assuming it to have a C_2 symmetry like the ground state $c\text{-}C_4H_4F_4$. As the C_2 axis is the only element of symmetry, this symmetry has to be conserved throughout the reaction. Therefore, the cleavage to give 2 CH_2CF_2 molecules would be symmetry allowed.

Even though the symmetry rules would not favor the formation of C_2F_4 and C_2H_4 through a sequential mechanism, it cannot be ruled out. Accordingly, the biradicals which can be formed are:

$$\cdot F_2C\text{-}CH_2\text{-}CH_2\text{-}CF_2 \cdot \qquad \text{(I)}$$

$$\cdot H_2C\text{-}CF_2\text{-}CF_2\text{-}CH_2 \cdot \qquad \text{(II)}$$

$$\cdot H_2C\text{-}CH_2\text{-}CF_2\text{-}CF_2 \cdot \qquad \text{(III)}$$
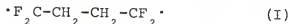
depending on which C-C bond in $(c\text{-}C_4H_4F_4)^*$ breaks first. The abundance of these three biradicals would depend on the energetics and the kinetics of the reactions leading to these biradicals and the availability of energy in $(c\text{-}C_4H_4F_4)^*$ to drive these reactions. The availability of energy for these reactions would depend on how much energy is channelled into the particular side of the molecule containing the C-C bond to be broken in $(c\text{-}C_4H_4F_4)^*$. The kinetics of the reactions accordingly depend on the energetics of the system and in particular the strengths of the bonds to be broken. A qualitative discussion of these two factors, energy availability and kinetics, is given below.

Even if energy is put into the molecule initially as

excitation energy, or via recombination of positive ions
with negative ions or electrons, most of it would end up
as vibrational energy via the usual route of internal
conversion to a high vibrational level of the ground
electronic state. There are nine active vibrations in
c-$C_4H_4F_4$.[72] Four of these vibrations, which are the most
active, are C-F stretches. Thus, the fluorine containing
side of the molecule will get more energy than the hydrogen
containing side.

A simplified Kassel type calculation using nine active
vibrations, an average excitation energy of 5 eV and bond
energies given in Chapter I shows that the fission of the
$F_2C...CF_2$ bond is three times more probable than the $H_2C...$
CH_2 bond. The combination of these two factors, the funnel-
ing of the energy to the fluorine containing side and rel-
atively larger rate constant for the breakage of the $F_2C...$
CF_2 bond, would help cleave this preferentially. Hence,
the biradical (I) would be more abundant than either (II)
or (III). These biradicals could undergo electronic re-
arrangement, with concurrent atom migration, leading to a
linear butene (or butene precursor) which could either be
stabilized or eliminate a CH_nF_{3-n} (n = 0-3). Alternatively,
the C_4 biradical could fragment to give two ethylenic
species. The amount of ethylenic products formed depends
on which of the three biradicals would undergo the scission
of the middle C-C bond to a greater extent.

The four factors which influence the scission of the

middle C-C bond in the biradical are the centrifugal forces, the bond energy of the middle C-C bond, the number of energy states available in that bond vibration and the energy content of the biradicals. The centrifugal forces pulling the biradical apart would be maximum in biradical (I) leading to the cleavage of the middle $\cdot H_2C-CH_2 \cdot$ bond and minimum in biradical (II) leading to the cleavage of the middle $\cdot F_2C-CF_2 \cdot$ bond. Because the bond strength of the middle bond in (I) is larger than in either (II) or (III) the centrifugal force enhances and bond strength inhibits the cleavage of the middle C-C bond. Furthermore, the middle bond in (I) will have a larger number of available states because the CH_2-CH_2 bond vibration frequency is higher than that of CF_2-CF_2, although it is quite possible that these C-C bond vibrations are not very active. Lastly, since the bond strength of $F_2C - CF_2$ bond is smaller than others, the biradical (I) would have more available (surplus) energy, on the average, than either (II) or (III). We could expect the inhibition due to bond energy would be at least partially cancelled by the excess energy of that biradical. Hence, the centrifugal effect would enhance the rupture of the middle bond in (I) more than in (II) or (III), and the formation of $CH_2 = CF_2$ would be larger than $C_2H_4 + C_2F_4$.

We have previously presented arguments that the reactions

$$C_4H_4F_4 \xrightarrow{\ e^-\ } C_2H_4^+ + C_2F_4 + e^-$$

$$\xrightarrow{\ e^-\ } C_2F_4^+ + C_2H_4 + e^-$$
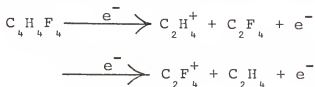
follow a concerted mechanism, while the reaction

$$C_4H_4F_4 \xrightarrow{\ e^-\ } C_2H_2F_2^+ + C_2H_2F_2 + e^-$$

goes through a sequential route as indicated.

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kcal/mole based upon the assumption that the observed ion/molecule reaction $C_2H_4^+ + C_2H_3F \quad C_3H_4F^+ + CH_3\cdot$ must be exothermic. Using $\Delta H_f^0(C_2H_3F) = -32.5$ kcal/mole and $\Delta H_f^0(CH_3\cdot) = +33.0$ kcal/mole as given by Jennings (ref. 13), and $\Delta H_f^0(C_2H_4^+) = 253$ kcal/mole as given in the NSRDS tables (ref. 18), we obtain 187.5 kcal/mole in essential agreement with Bowers. This result clearly depends on the accuracy of the thermodynamic input data, as well as the validity of Bower's assumption.

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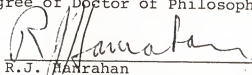
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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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